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**ELECTRICAL AND ENVIRONMENTAL
STUDIES OF CONDUCTING POLYMERS**

Dr. Mark A. Druy
GTE Laboratories Inc.
Waltham, MA 02254

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The objective of this research was to present a clear and defined strategy toward the synthesis of environmentally stable conducting polymers, paying particular attention to the influence of the dopant on the electrical conductivity, environmental stability, and the dielectric properties. This involves a fundamental understanding of the molecular basis for the electrical properties and the interaction of the dopant with the polymer backbone.

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On the basis of an investigation into the kinetics of the degradation of electrical conductivity in two conducting polymer systems, i.e., polythiophene and polypyrrole, one can make the following conclusions.

First, and most important, a conducting polymer system was identified which is thermally stable in an inert atmosphere and whose degradation of conductivity when exposed to air follows first order kinetics. Specific examples are polypyrrole/toluene sulfonate and a multicomponent system comprising polypyrrole, toluene sulfonate, and a processible polymeric component. Other anions commonly used in synthesizing polypyrrole, namely, tetrafluoroborate, hexafluorophosphate, trifluoromethyl sulfonate, and perchlorate were also examined and these systems did not obey first order degradation kinetics in laboratory air. Tetrafluoroborate and perchlorate doped polypyrrole were found to lose conductivity when heated in an inert atmosphere, thus these materials may not be thermally stable. Two different processes for the degradation of conductivity were established. One follows first order reaction kinetics and the other appears to be a more complex process. The degradation mechanism which follows first order kinetics may involve reaction of the delocalized carbonium ion along the polymer backbone with oxygen or water. Polypyrrole/toluene sulfonate (prepared in laboratory air) is an example of this phenomenon. The other degradation mechanism is most likely a combination of two or more processes such as reaction of the polymer backbone with the dopant anion and reaction of the polymer backbone with oxygen or water. Additionally, it is possible that the dopant species itself might undergo thermal degradation and the products of this degradation could react with the polymer backbone. Polypyrrole/perchlorate is an example of this degradation mechanism.

The capability to predict adequately the environment stability of a conducting polymer on the basis of a kinetic treatment of accelerated life tests was also demonstrated for the first time. The data obtained and analyzed for polypyrrole/toluene sulfonate suggests an order of magnitude loss of conductivity for every 3.2 years exposure to air at ambient conditions. Since the degradation mechanism appears to follow first order reaction kinetics and may involve the reaction of the delocalized carbonium ion backbone with oxygen or water, it should be possible to improve the environmental stability with encapsulation. The kinetics of the degradation of the polypyrrole multi-component system suggests this has occurred. This material exhibits a 30% lower rate constant for degradation at room temperature than the polypyrrole toluene sulfonate system and has the same activation energy, thus suggesting a one order of magnitude loss of conductivity for every 4.6 years exposure to air at room temperature.

Another conducting polymer system, namely multicomponent polythiophene/polyTHF was found to be less stable with respect to polypyrrole and it follows a multi-order degradation process in laboratory air. The rate of degradation above 80°C is significantly higher than the polypyrrole systems investigated. This was postulated to be as a result of the degradation of the polyTHF component at temperatures in excess of 90°C.

The dielectric properties of the above materials were investigated over the frequency rate from 1-100 GHz. The dielectric behavior was consistently found to be independent of the type of anion present in these conducting polymer systems. In other words, the dielectric properties seemed to be controlled by the bulk conductivity of the samples. Polypyrrole as thin films exhibited properties similar to those of a weak metal, with loss components of the dielectric constant in the range of 10^3 and high reflection coefficients. When polypyrrole was post processed into a composite with a polyurethane it showed significant improvement in its ability to function as a broad band absorber and the reflection coefficients were released.

FOREWORD

The following final report describes work performed on Navy Contract No. N62269-84-0274, "Electrical and Environmental Studies of Conducting Polymers". The work accomplished and reported herein was performed by GTE Fundamental Research Laboratories, Waltham, MA. The program was monitored by Dr. Leonard J. Buckley of the Naval Air Development Center, Aero Materials Division.

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Introduction

This report is organized into several sections and each section is a self contained entity including experimental, results, and a discussion section. Section 8 provides recommendations for future investigations in conducting polymers.

The environmental stability of the following systems was investigated:

1. Polypyrrole	Section 1
2. Multicomponent Systems of Polypyrrole	Section 2
3. Polythiophene/PolyTHF	Section 3

The synthesis of some additional polymeric systems which were expected to be conducting was attempted and these include:

1. Multicomponent Systems of Polyfuran	Section 4
2. Polycarbazole	Section 5

Section 6

In addition it was attempted to incorporate metal containing anions such as hexachloroiridate ($IrCl_6^{2-}$) and tetrachloroferrate ($FeCl_4^-$) into polypyrrole in the hope of observing the effect of these anions on the dielectric properties and stability of the polypyrrole.

Section 7

The dielectric properties of the polypyrrole system were investigated over a broad frequency range (1-100 GHz) in order to determine the effect if any of the anion on the dielectric properties of polypyrrole. The systems investigated were the following:

1. Polypyrrole/PTS
2. Polypyrrole/BF_4
3. Polypyrrole/CF_3SO_3
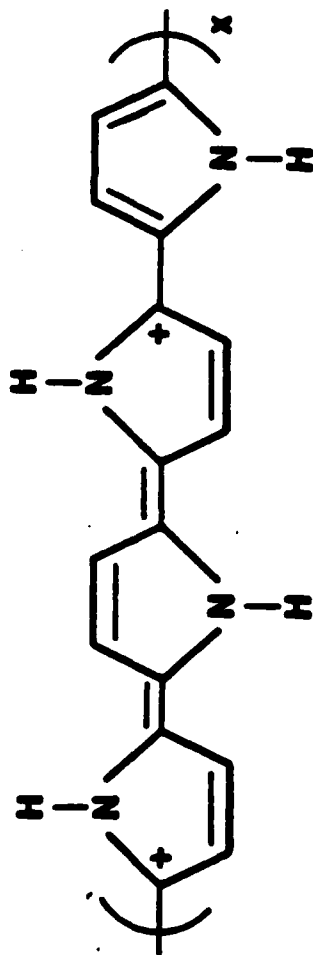4. Polythiophene/PolyTHF Multicomponent System

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Section 1: Polypyrrole

The development of conducting polymers can be traced to the mid-1970's when researchers at the University of Pennsylvania reported that films of polyacetylene could be rendered conducting by reaction (doping) with a suitable electron-withdrawing group or electron-donating group (1). Since that time, several other conducting polymers have been discovered (2). One class of these conducting polymers is the polyheterocycles such as polypyrrole and its chalcogen analogues. Polypyrrole is normally synthesized electrochemically (3) and as a result of the simultaneous oxidation and polymerization of the pyrrole monomer, the conducting form of the polymer which is generated is an oxidized backbone (see Figure 1) with a delocalized positive charge in the pi electron system. Electrical conduction is thought to occur by conduction of these "holes" (4). In order to maintain charge neutrality an anion from the electrolyte is incorporated into the polymer. Typical anions which are incorporated are perchlorate (ClO_4^-), tetrafluoroborate (BF_4^-), trifluoromethyl sulfonate ($CF_3SO_3^-$), hexafluorophosphate (PF_6^-), and p-toluene sulfonate (PTS).

Polypyrrole (in its oxidized conducting form) has been found by many investigators to possess reasonable stability in air towards the degradation of conductivity and been the subject of thermal experiments in which it was found to be stable to mass loss up up to 180 °C (5). Additionally Salmon et al observed that polypyrrole doped with perchlorate, tetrafluoroborate, and hexafluorophosphate lost conductivity and decomposed at ca > 150 °C in air (5) and toluene sulfonate containing films did not decompose until 280 °C. Although a dependence of stability on anion was reported, it was not evident from this study whether the dependence was due to a decreased reactivity of the dopant/polymer system with oxygen and moisture or due to decreased reactivity between dopant and polymer themselves. In other words, was an intrinsic or extrinsic stability measured?

Detailed investigations have been carried out at GTE Laboratories to identify the role of the dopant anion in the degradation of electrical conductivity in polypyrrole. In order to determine if the conductivity degraded as a result of dopant degradation or dopant reaction with the polymer backbone, polypyrrole was heated in an inert atmosphere and its conductivity was measured before and after heating. The kinetics of the degradation process were also followed in air in order to identify the nature of the degradation process. Our findings further establish the inherent stability of polypyrrole and the importance of the dopant in determining the environmental and intrinsic stability of conducting polymers.

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Figure 1: Structure of oxidized and electronically conducting polypyrrole.

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Thus, the focus of this section of the report is to present this investigation of the inherent stability of the polypyrrole system and the role of the dopant in the degradation process and to address questions regarding the kinetics of the degradation process of conductivity in polypyrrole.

Experimental

Pyrrole monomer (Aldrich) was distilled under nitrogen before use and simultaneously oxidized and polymerized in a three compartment cell under galvanostatic control. The current density was 0.6-0.8 mamp/cm^2. The solvents and electrolyte combinations were as follows: 1 M Lithium Perchlorate (LiClO$_4$)/THF, 0.3 M tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$)/THF, 0.25 M Tetraethylammonium p-toluene sulfonate (Et$_4$NPTS)/Acetonitrile or Propylene Carbonate), 0.25M Tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$)/THF, and 0.25M Lithium Trifluoromethyl sulfonate (LiCF$_3$SO$_3$)/THF. Lithium Perchlorate (G. F. Smith Co.) was dried at 105 C under dynamic vacuum for 36 hours and then melted and cooled under dynamic vacuum prior to use. Tetrabutylammoniumtetrafluoroborate, tetrabutylhexafluorophosphate, (both Southwestern Analytical), and lithium trifluoromethyl sulfonate (Alfa) were dried overnight at 105 C under dynamic vacuum before use. Tetraethylammonium p-toluene sulfonate (Aldrich) was used as received. Tetrahydrofuran (THF) and Acetonitrile were dried as previously described (6,7). Propylene Carbonate (Burdick and Jackson) was used as received. All electrochemical polymerizations were performed in an inert atmosphere glove box except as discussed below. Conductivity measurements were performed using a four probe arrangement and a pressure contact was made between the platinum wires and the film.

The doped samples were heated in an inert atmosphere and in laboratory air. The following dopants were evaluated: ClO$_4^-$ (perchlorate), BF$_4^-$ (tetrafluoroborate), and CH$_3$C$_6$H$_4$SO$_3^-$ (p-toluene sulfonate), PF$_6^-$ (hexafluorophosphate), and CF$_3$SO$_3^-$ (trifluoromethyl sulfonate). The samples were mounted via a pressure contact to a glass four probe cell which was fitted with a ground joint and a stopcock such that the cell could be evacuated and backfilled with the desired atmosphere. Each doped sample was heated in an oil bath while exposed to laboratory air. The four probe resistance was monitored in situ and the experiment was carried out for 900 minutes. The samples were heated at 100, 125, and 150 degrees centigrade and a fresh sample was used for each heating run. The four probe resistance of the samples was also monitored at room temperature (22 C) in laboratory air.

Results

Many investigators have observed the effect of dopant on the physical properties of polypyrrole. In particular, Salmon et al (8) observed that kinetics of the electrochemical switching response were influenced by the choice of anion. It was postulated that the size of the anion and its ability to diffuse in and out of the film affected the shape of the cyclic voltammogram and thus the kinetics of the oxidation and reduction of polypyrrole.
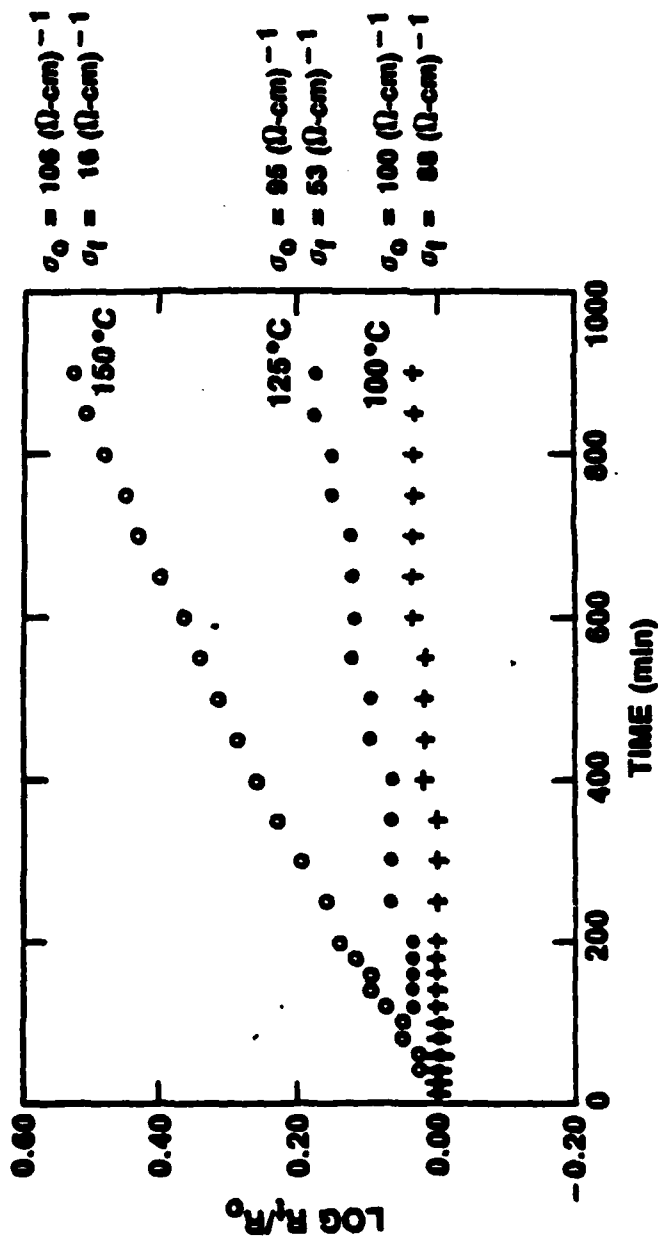
Additionally, as was previously mentioned, the thermal stability of polypyrrole was influenced by the choice of anion. More recently, Diaz observed a dependence of the mechanical properties on the choice of anion. Polypyrrole synthesized in the presence of perchlorate and tetrafluoroborate tended to be less ductile and weaker than Polypyrrole synthesized in the presence of toluene sulfonate (5). The authors of the previous study suggested that chemical differences between the anions could be responsible for the various properties which were observed to depend on the choice of the anion. The question which therefore arises is what is unique about the toluene sulfonate anion and its interaction with the polypyrrole backbone such that the complex exhibits a high degree of thermal stability ? The effect of the counterion on the thermal stability might even be more indirect than mentioned above. For example, the effect of the anion might be to alter the crystallinity of the polymer/dopant complex, alter the content of chemical defects, or extent of backbone oxidation. All of these may effect the reactivity of the dopant/polymer system to the environment and its thermal stability. It was our intention to critically evaluate the process which results in a loss of conductivity when polypyrrole is exposed to ambient conditions, heated in an inert atmosphere, and heated in air and to correlate this process with the counterion.

Figure 2 shows the data for the combination of polypyrrole and toluene sulfonate. Similar data was obtained from the other samples. This figure contains the data from the runs at 100, 125, and 150 degrees. The data is plotted as a function of log R_t/R_0 vs time (min). R_t represents the resistance of the sample at the temperature of the experiment at a given time. R_0 represents the resistance of the sample at the temperature of the experiment at time zero. The data is fit to a linear function, i.e.,

$$\log R_t/R_0 = kt, \qquad (1)$$

where k is the slope of the line and the rate constant for the degradation process. In this case the y intercept is assumed to be zero, i.e, $\log R_t/R_0 = 0$ when t=0. The natural logarithm of each rate constant is then plotted as a function of inverse temp (in degrees Kelvin). By doing this we are

Figure 2: Log R_t/R_o vs time (min) exposed to air at elevated temperature for polypyrrole/toluene sulfonate. R_t = resistance of the sample at the temperature of the experiment at a given time. R_o = resistance of the sample at the temperature of the experiment at time zero.

assuming first order reaction kinetics. The plot is fit to equation 2

$$k = A\, e^{(-E/RT)} \text{ or } \ln k = -E/RT \quad (2)$$

where R is 0.00197 kcal/mol.K, E the activation energy for the degradation process, and T is the temperature in degrees Kelvin. Thus the slope of this line is the activation energy for degradation of the conductivity in air. The rate constants for polypyrrole doped with the toluene sulfonate, tetrafluoroborate, perchlorate, hexafluorophosphate, and trifluoromethyl sulfonate anions are listed in Table 1 for each of the four temperatures. The plot of ln k vs inverse temperature is shown in Figure 3-6 for polypyrrole/toluene sulfonate, polypyrrole/tetrafluoroborate, and polypyrrole/perchlorate, polypyrrole hexafluorophosphate, and polypyrrole trifluoromethyl sulfonate, respectively. The data shown in Figure 3 are for a polypyrrole/toluene sulfonate film which was made in laboratory air. Otherwise all other samples were made in an inert atmosphere glove box using rigorously dried solvents and electrolytes. In a separate experiment polypyrrole/toluene sulfonate was prepared under identical conditons as the other samples and the plot of ln k vs inverse temperature is shown in figure 7. Its non-linear kinetic behavior was found to be similar to that of the perchlorate, tetrafluoroborate, and hexafluorophosphate doped samples.

In a separate experiment, polypyrrole/toluene sulfonate (made in laboratory air), polypyrrole/tetrafluoroborate, and polypyrrole/perchlorate were heated in sealed tubes in a dry nitrogen/vacuum atmosphere. The conductivities of the samples were measured before and after heating and the samples were heated at 100, 125, and 150 C. Table 2 shows the results of this experiment.

Discussion

From examination of the data in figures 3-7, we conclude the following points. The first is that the behavior of the polypyrrole/toluene sulfonate (made in the presence of laboratory air is first order and that all the other systems were not first order in their degradation of the conductivity. In other words, the degradation of the conductivity when polypyrrole/toluene sulfonate is exposed to air appears to be a process which follows first order reaction kinetics; i.e., reaction of the polymer backbone with air. On the other hand, the degradation of conductivity of polypyrrole/tetrafluoroborate and polypyrrole/perchlorate does not follow first order reaction kinetics. Consideration of the results in Table 2 suggest that in the case of tetrafluoroborate and perchlorate doped polypyrrole, there is another reaction which results in the degradation of conductivity when these materials are heated in an inert atmosphere. It should be noted that under identical conditions, the conductivity of toluene sulfonate doped polypyyrole did not degrade (see Table 2). The causes of the decrease of conductivity in perchlorate and tetrafluoroborate doped

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Rate constants for polypyrrole/toluene sulfonate, polypyrrole/tetrafluoroborate, polypyrrole/perchlorate, polypyrrole trifluoromethyl sulfonate, and polypyrrole hexafluorophosphate obtained from fitting data to Equation 1 (see text).

Sample	Temp. °C	Rate Constant, k min^{-1}
polypyrrole/toluene sulfonate	22	5.9×10^{-7}
"	100	6.8×10^{-5}
"	125	1.8×10^{-4}
"	150	5.9×10^{-4}
polypyrrole/tetrafluoroborate	22	2.1×10^{-6}
"	100	1.2×10^{-4}
"	125	4.2×10^{-4}
"	150	5.5×10^{-4}
polypyrrole/perchlorate	22	5.7×10^{-6}
"	100	9.2×10^{-5}
"	125	2.4×10^{-4}
"	150	3.3×10^{-4}
polypyrrole/CF_3SO_3	22	-
"	100	8.42×10^{-5}
"	125	1.57×10^{-4}
"	150	3.36×10^{-4}
polypyrrole/PF_6	22	7.0×10^{-7}
"	100	6.63×10^{-5}
"	125	1.16×10^{-4}
"	150	1.75×10^{-4}
polypyrrole/toluene sulfonate[*]	22	6.0×10^{-7}
"	100	1.64×10^{-4}
"	125	2.29×10^{-4}
"	150	4.33×10^{-4}

[*] Prepared in the dry box

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Figure 3: ln k vs 1/T (T = K) for polypyrrole/toluene sulfonate. Rate constants, k, are from
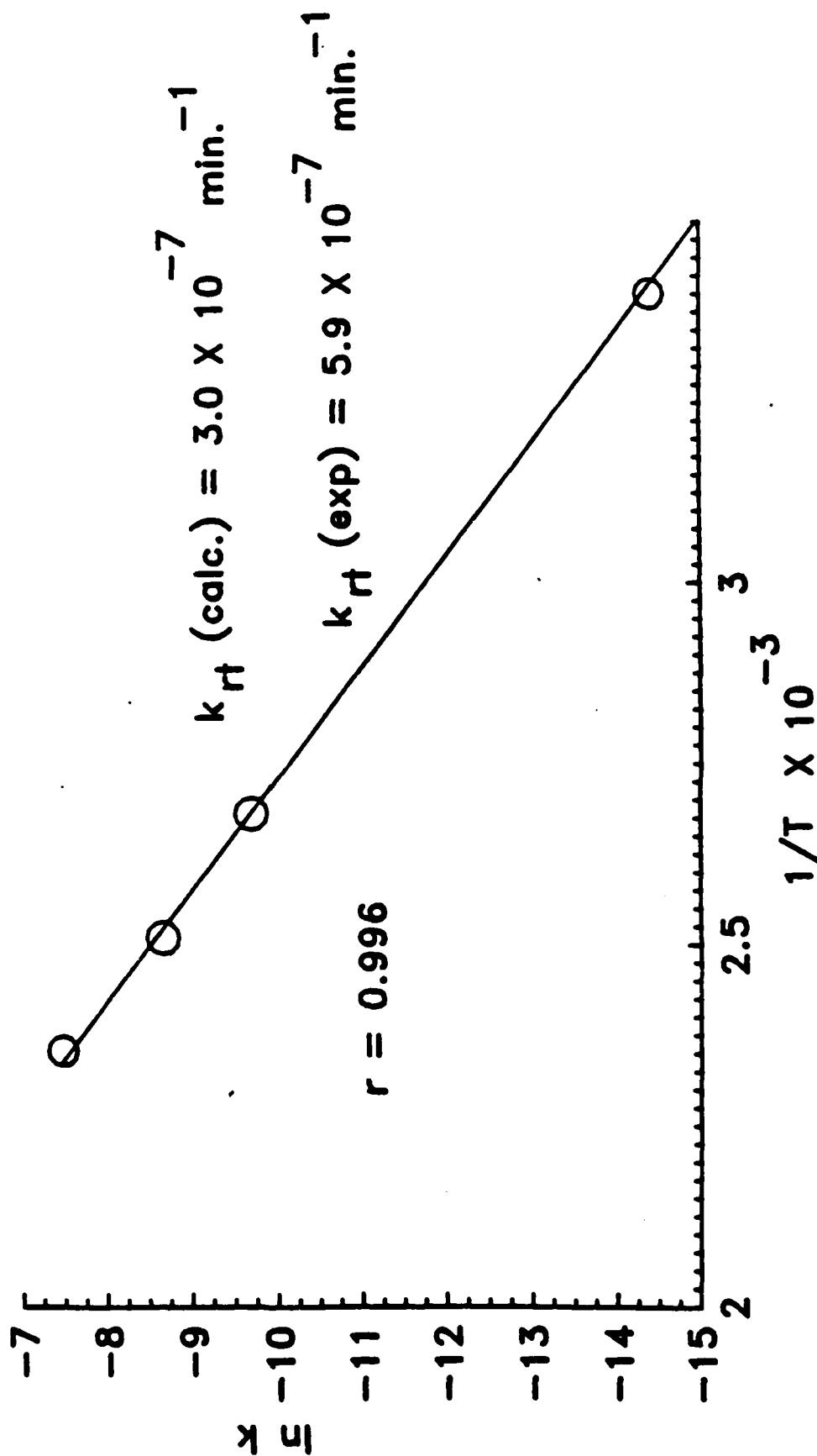Table 1. r = correlation coefficient for line drawn through points.

Figure 4: ln k vs 1/T (T = K) for polypyrrole/tetrafluoroborate. Rate constants, k, are from Table 1.

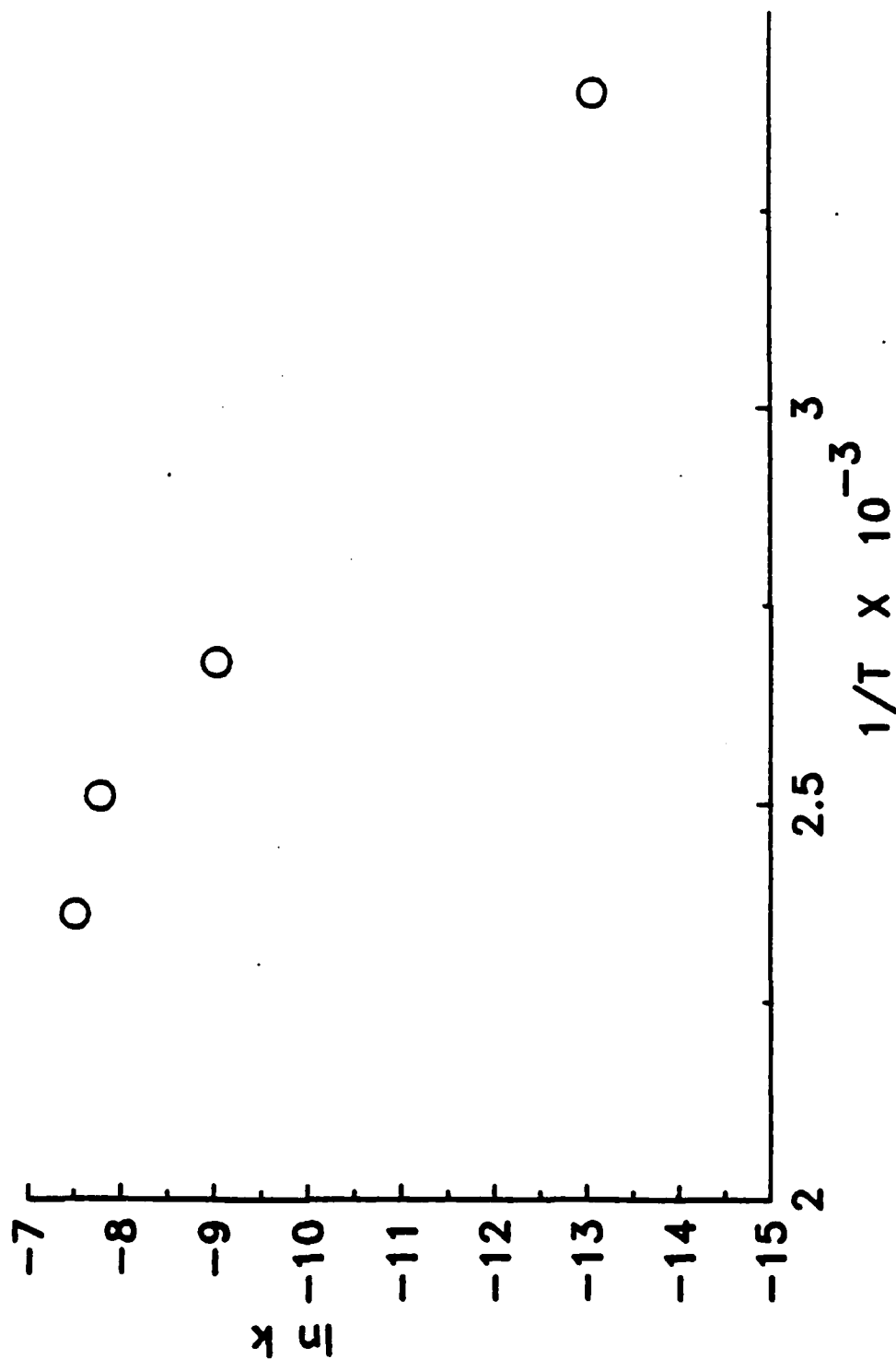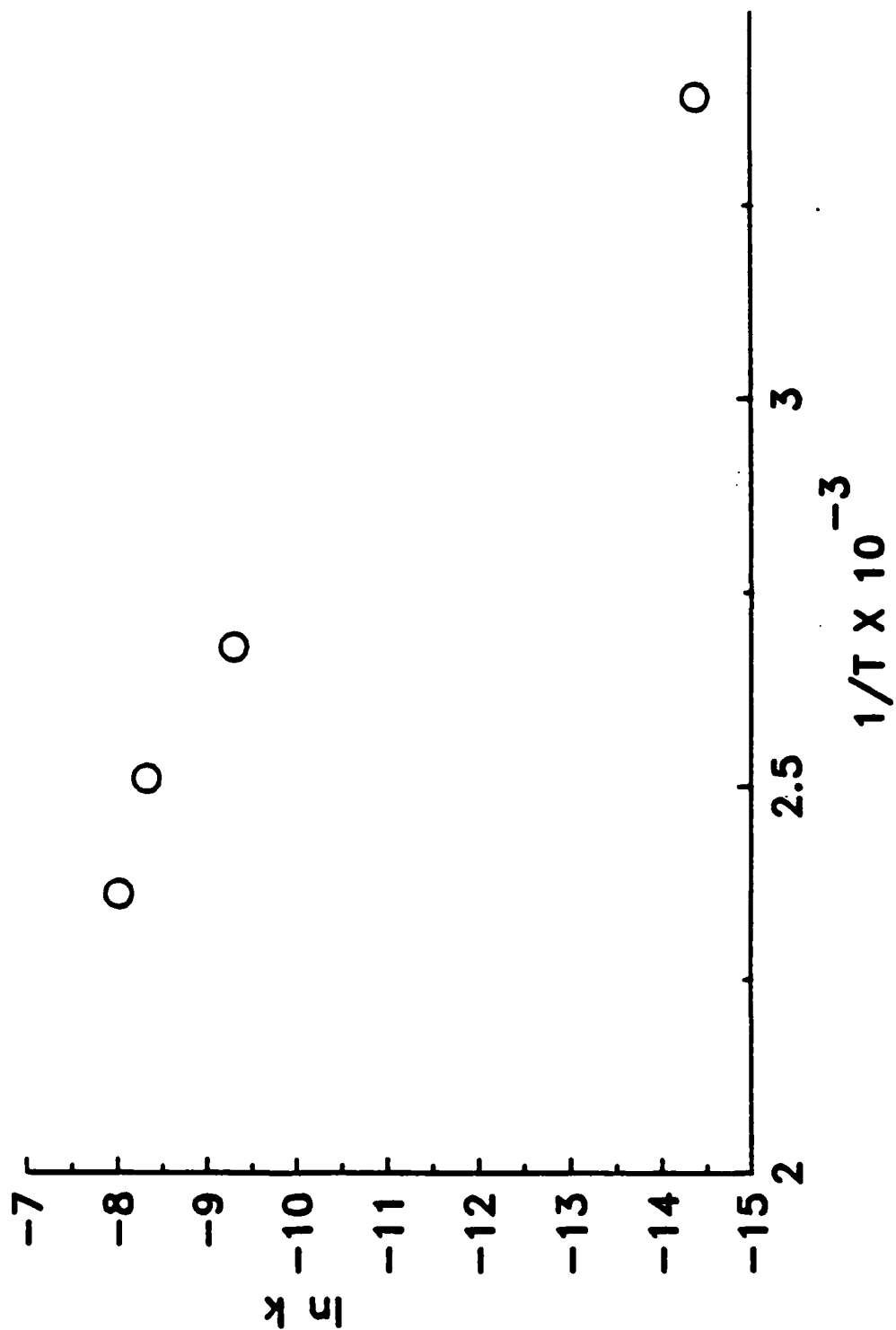Figure 5: ln k vs 1/T (T = K) for polypyrrole/perchlorate. Rate constants, k, are from Table 1.

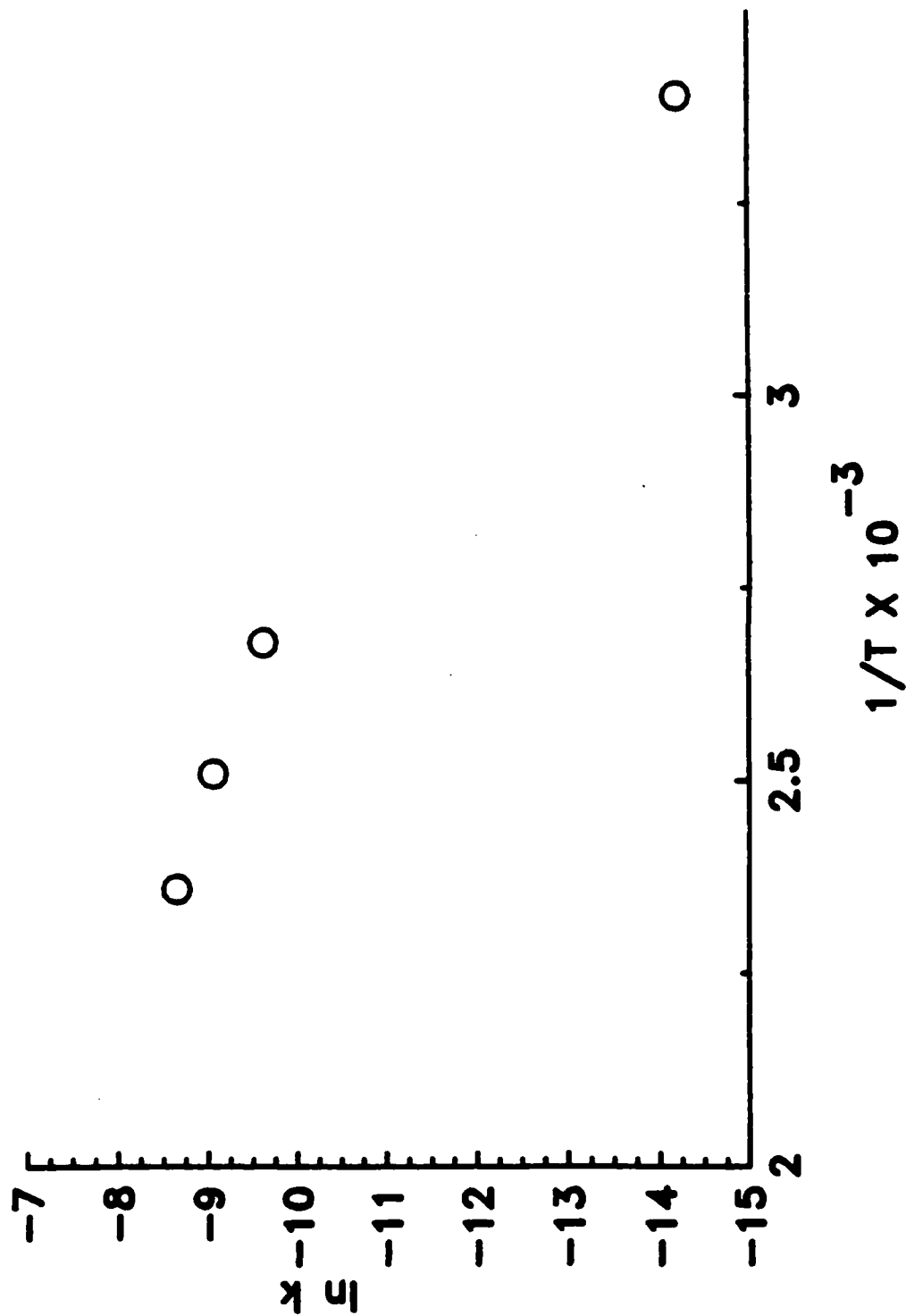Figure 6: ln k vs 1/T (T = K) for polypyrrole/hexafluorophosphate. Rate constants, k, are from Table 1.

Figure 7: ln k vs $1/T$ ($T = K$) for polypyrrole/toluene sulfonate (prepared in dry box). Rate constants, k, are from Table 1.

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TABLE II

Conductivity before and after heating in nitrogen for 900 minutes of polypyrrole toluene sulfonate and polypyrrole perchlorate.

Sample	Temperature	Conductivity Before	$(ohm-cm)^{-1}$ After
Polypyrrole PTS	100	31	40
"	100	71	74
"	125	64	69
"	125	122	123
"	150	35	40 (4 days)
"	150	25	28
"	150	62	69 (4 days)
"	200	65	42
Polypyrrole Perchlorate	100	98	70
"	125	70	35
"	125	49	19 (4 days)
Polypyrrole Tetrafluoroborate	100	85	117
"	125	125	165
"	125	84	96
"	150	96	90
"	150	115	90

polypyrrole when it is heated in an inert atmosphere may be due to degradation of the dopant and subsequent reaction of the products of the degradation with the polymer backbone or a reaction between the dopant and polymer backbone which results in a loss of conductivity.

Since the behavior of the polypyrrole/toluene sulfonate follows first order reaction kinetics, we can calculate the activation energy for the degradation process from Equation 2 and the slope of the line in Figure 3. The calculated activation energy is 13 kcal/mol. Knowing the activation energy and a rate constant for the degradation at a specific temperature, we can calculate a rate constant for the degradation of the conductivity at room temperature. The calculated rate constant is 3.0×10^{-7} min^{-1}. Thus, there is very good correlation between the calculated and experimental (see Table 1) rate constants.

The experimental room temperature rate constant represents an one order of magnitude loss in conductivity for every 3 years exposure to laboratory air for polypyrrole/toluene sulfonate which was synthesized in laboratory air.

Additionally it should be mentioned that the effect of the counterion on the intrinsic and extrinsic stability could be more indirect than mentioned above. For example, the effect of the anion might be to alter the crystallinity of the polymer/dopant system, alter the content of chemical defects, or extent of backbone oxidation. All of these may effect the reactivity of the dopant/polymer system to the environment and its thermal stability.

Summary

The effect of dopant on the kinetics of the degradation of electrical conductivity of polypyrrole when it is heated in laboratory air and exposed to laboratory air at ambient conditions was investigated. In particular two different kinetic processes for the degradation of conductivity were found. One follows first order reaction kinetics and the other appears to be a more complex process. The degradation mechanism which follows first order kinetics may be reaction of the delocalized carbonium ion along the polymer backbone with oxygen or water. Polypyrrole/toluene sulfonate (prepared in laboratory air) is an example of this phenomenon. The other degradation mechanism is most likely a combination of two or more processes. One is the reaction of the polymer backbone with the dopant anion and the other is the reaction of the polymer backbone with oxygen or water.

Additionally it is possible that the dopant species itself might undergo thermal degradation and the products of this degradation could react with the polymer backbone. Polypyrrole/perchlorate is an example of this degradation mechanism.

It was also demonstrated for the first time the capability to predict adequately the environmental stability of a conducting polymer on the basis of a kinetic treatment of accelerated life tests. The data obtained and analyzed for polypyrrole/toluene sulfonate suggests an one order of magnitude loss of conductivity for every three years exposure to air at ambient conditions. Since th degradation mechanism appears to follow first order reaction kinetics and may involve the reaction of the delocalized carbonium ion backbone with oxygen or water, it should be possible to improve the environmental stability with encapsulation.

Section 2: Multicomponent Systems of Polypyrrole

The multicomponent system contains a non-conducting component which increases the ductility and processibility of polypyrrole.

In order to determine whether or not the environmental stability was enhanced or compromised as a result of the incorporation of the second component, a kinetic study similar to that in section 1 was performed. Figure 8 shows the results of the kinetic study at 100, 125 , and 150 C, room temperature data was also obtained and the rate constants for the four temperatures are summarized in table 3.

TABLE 3

Rate constants for multicomponent polypyrrole toluene sulfonate obtained from fitting data to Equation 1 (see text).

Temp °C	Rate Constant, k min^{-1}
22	4.1×10^{-7}
100	3.7×10^{-5}
125	1.3×10^{-4}
150	2.5×10^{-4}

A plot of ln k vs inverse temperature is shown in Figure 9. As the data indicates, the

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Figure 8: Log R_t/R_o vs time (min) exposed to air at elevated temperature for polypyrrole multicomponent system. R_t = resistance of the sample at the temperature of the experiment at a given time. R_o = resistance of the sample at the temperature of the experiment at time zero.
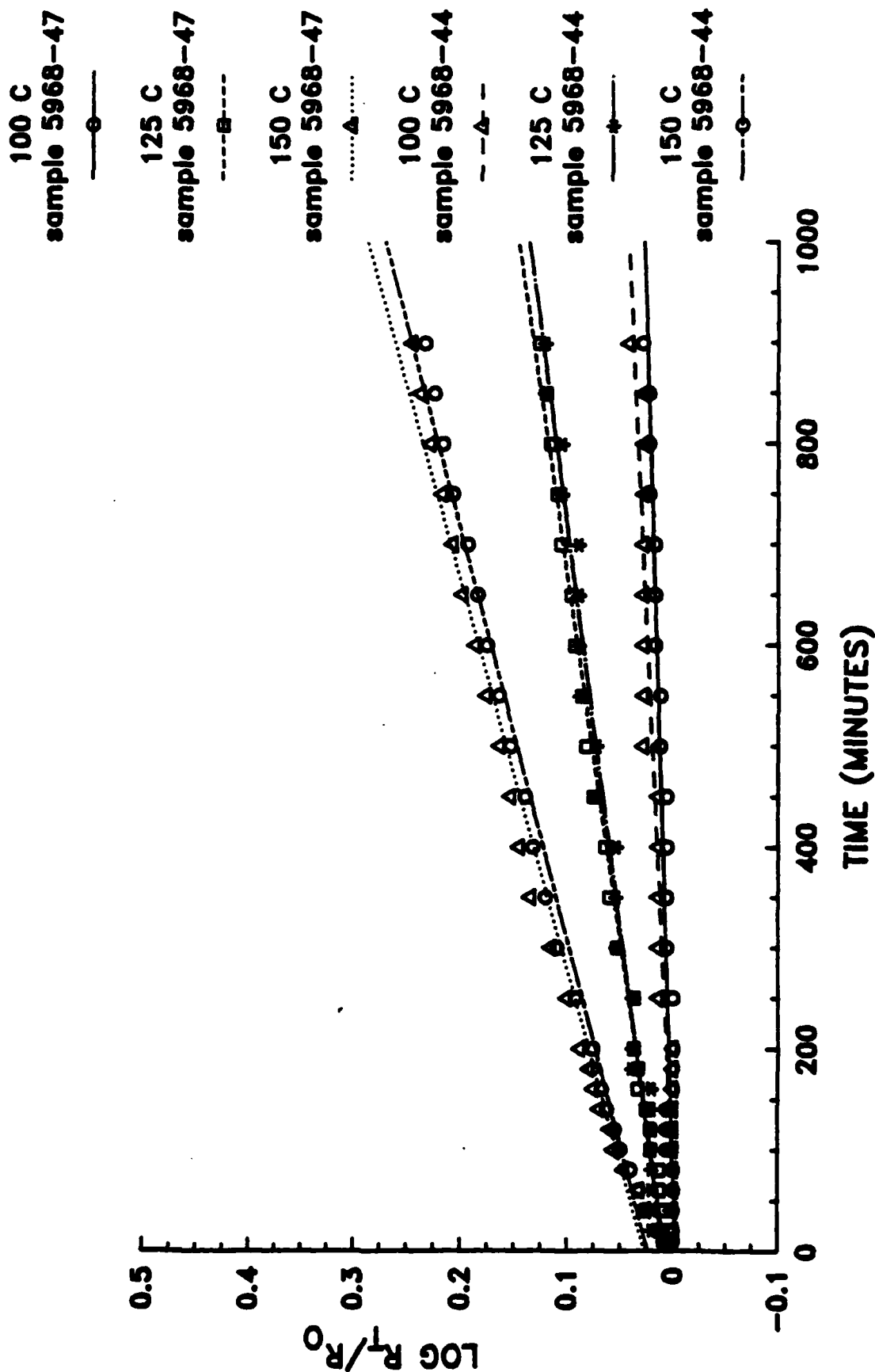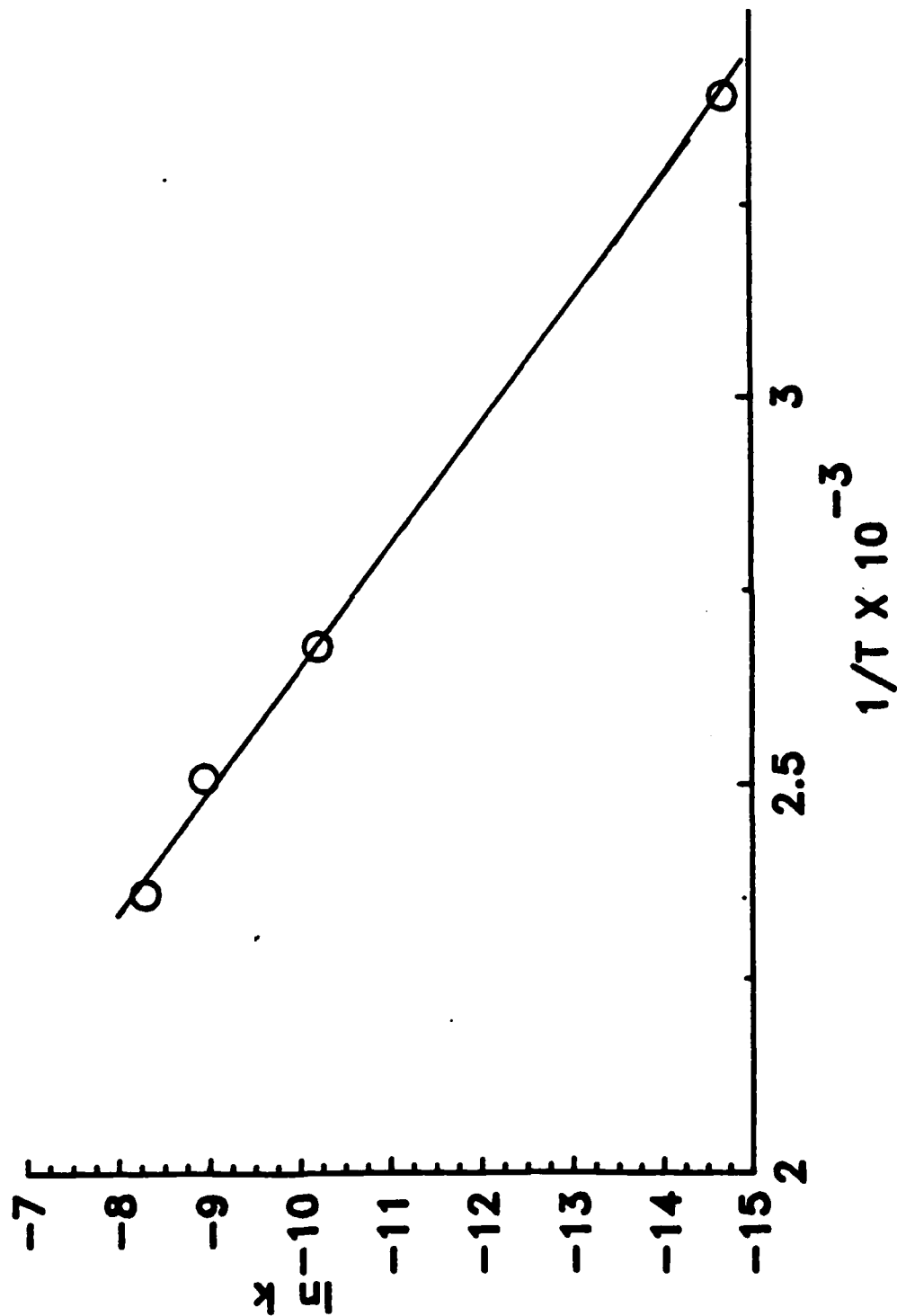
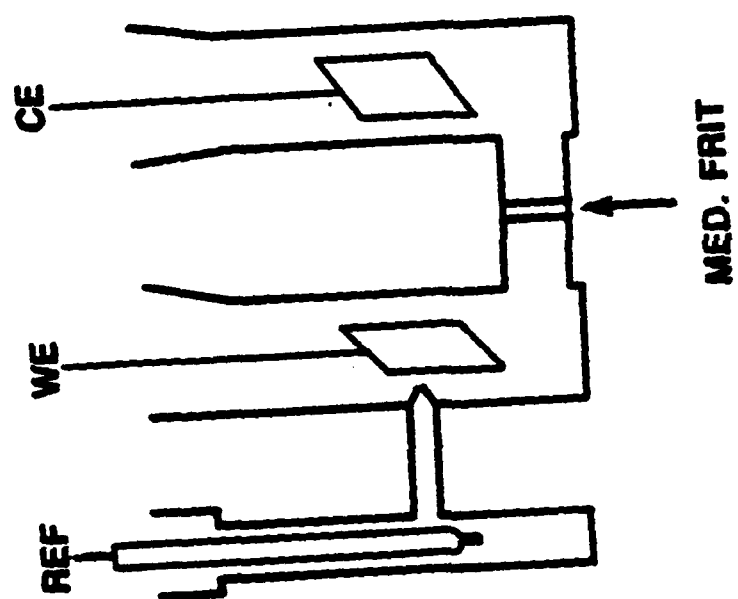Figure 9: ln k vs 1/T (T = K) for polypyrrole multicomponent system. Rate constants, k, are from Table 3.

multicomponent system appears to be more stable than polypyrrole. Although the activation energy calculated (12.5 kcal/mole) for the degradation process is similar to that of the polypyrrole/toluene sulfonate system, the overall magnitude of the rate constants are less than that for polypyrrole/toluene sulfonate. If diffusion of oxygen or moisture is a factor which causes the conductivity to decrease, then the incorporation of the non-conducting component has resulted in a slowing down of that process. One possible mechanism which would result in the lowering of the rate constants involves a cooperative effect in the multicomponent system between the non-conducting component, the polypyrrole chain, and the toluene sulfonate anion. The cooperative effect would result in an increased microcrystalline order which would impede the diffusion of oxygen or moisture which subsequently would lead to a degradation of the electrical conductivity.

Section 3: Polythiophene/PolyTHF Multicomponent System

Another polyheterocycle which has demonstrated good oxidative stability is polythiophene. Polythiophene, however, has rather poor mechanical properties. In fact it is very difficult to synthesize polythiophene as a free-standing film (> 10 microns thick). Most attempts to electrochemically synthesize polythiophene result in intractable powders which are deposited on the surface of an electrode (7,9). Only by keeping the current density at 10 uA/cm^2 is it possible to peel off a fragile free-standing film (7). Since the conductivity of polythiophene is rather stable in air, attempts to improve its mechanical properties and processibility were warranted. In a previous investigation researchers were successful in altering the growth morphology of polythiophene and as a result improved its mechanical integrity such that flexible freestanding films could be readily obtained (6). This was accomplished by synthesizing a polythiophene/polyTHF multicomponent system. The synthesis of this material is described below and following that is the report of the kinetics of the degradation of electrical conductivity upon air exposure.

A three compartment electrochemical cell was used for the electrochemical synthesis of a polythiophene/polyTHF multicomponent system. Figure 10 shows this cell. A Ag/Ag+ reference electrode (+0.3 V vs SCE) which was used to monitor the working electrode potential during the galvanostatic synthetic process. The working electrode was a 4 cm x 2.5 cm platinum working electrode, and a nickel mesh counter electrode was used. The cell was filled with 50 ml of a 1M solution of lithium perchlorate in tetrahydrofuran. The lithium perchlorate (G.F. Smith Co) had been previously dried at 110 degrees C in dynamic vacuum for 36 hours, and then melted and allowed to cool under dynamic vacuum. The tetrahyrofuran (Fisher HPLC) was refluxed over lithium aluminum hydride, collected, and transferred under nitrogen flow to a flask containing benzophenone and sodium metal. The THF was degassed using free-thaw cycles on a vacuum system. THF was transferred from this container to another flask which could be brought into a

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Figure 10: Electrochemical cell for the polymerization of bithiophene and THF.

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Vacuum Atmosphere dry box using vacuum distillation techniques. The cell was assembled in the dry box and the platinum electrode was made the anode during a controlled current process. A current of 0.8 mA/cm^2 was passed for a duration of 30 coulombs. During this time, oxidation of THF occurred at the platinum electrode and the solution became more viscous.

After the passage of 30 coulombs, the cell was turned off and 0.1 gm of bithiophene was added to the working electrode compartment. The bithiophene (Eastman) was previously sublimed under vacuum. The working electrode was again made the anode for an additional 30-50 coulombs passed at a current density of 0.8 mA/cm^2. During this time the working electrode potential was monitored and was found to be 0.7 V vs Ag/Ag$^+$, indicative of bithiophene oxidation and polymerization (7). A dark green film formed on the electrode during this second electrolysis. After the second electrolysis period the electrode was removed from the cell and was scraped with a knife inorder ot remove excess polyTHF. The electrode was immersed in a beaker containing THF. This was done in order to dissolve any residual polyTHF on the surface of the electrode. The electrode was then removed from the dry box and a flexible free-standing film 40-120 microns thick was peeled off the electrode. These films were washed a second time in THF and then dried under vaccuum.

The conductivity of the films at room temperature and at elevated temperatures was measured using a 4 probe pressure contact. All electrochemical measurements and syntheses were carried out with a PAR model 174 signal programmer, 173/179 potentiostat/ galvanostat/coulometer, and a houston instruments XY recorder.

Evaluation of the Environmental Stability of Polythiophene/PolyTHF

The experimental procedure was the same as described in section 1. The multicomponent system was heated at 80, 100, and 125 degrees centigrade.

The log R_t/R_o vs time data is shown in figure 11. The rate constants are listed in table 4 and the plot of ln k vs inverse temperature is shown in figure 12.

Figure 11: Log R_t/R_0 vs time (min) exposed to air at elevated temperature for polythiophene/polyTHF multicomponent system. R_t = resistance of the sample at the temperature of the experiment at a given time. R_0 = resistance of the sample at the temperature of the experiment at time zero.
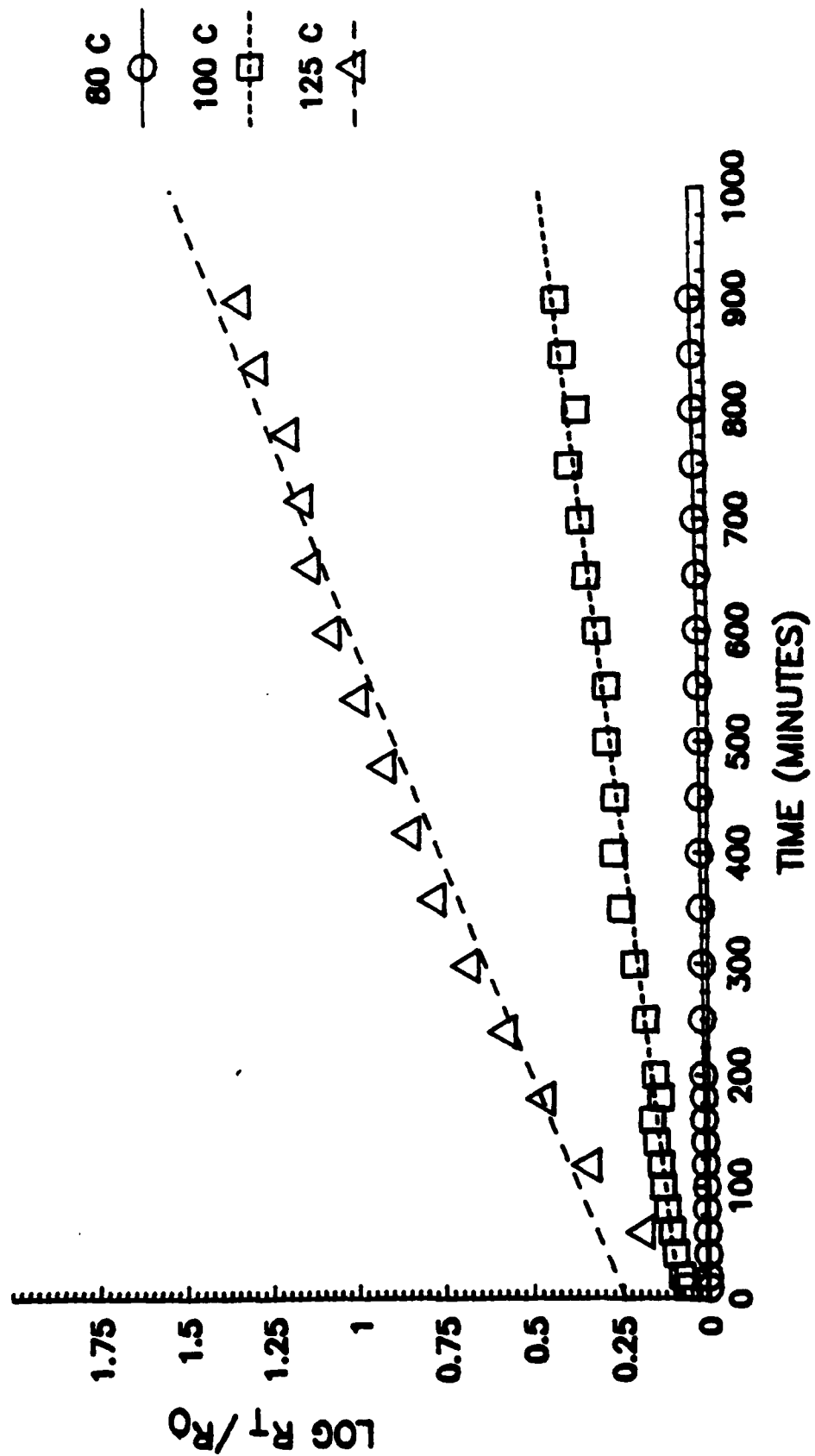
22

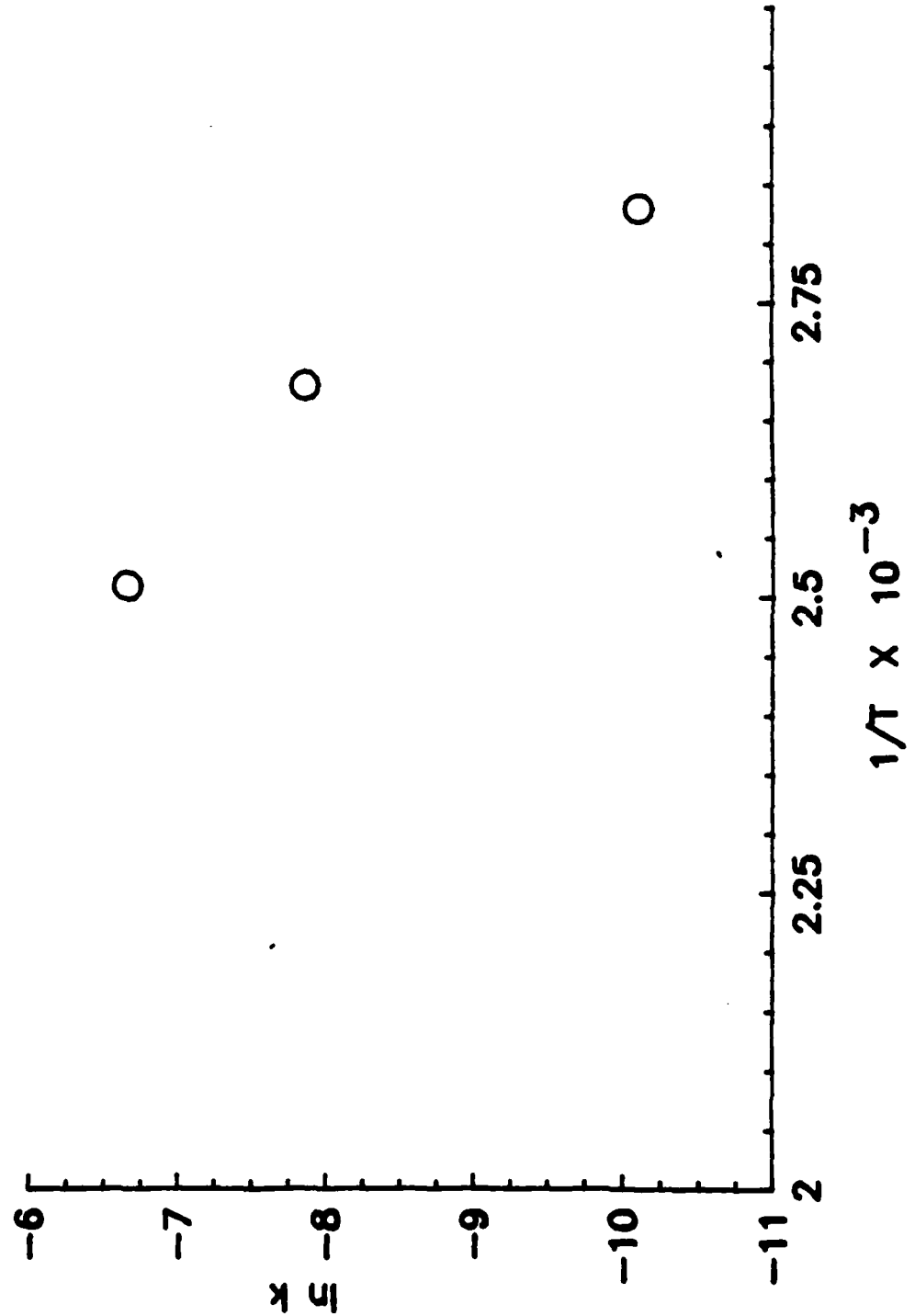Figure 12: ln k vs 1/T (T = K) for polythiophene/polyTHF multicomponent system. Rate constants, k, are from Table 4.

TABLE 4

Rate constants for polythiophene/polyTHF multicomponent system obtained from fitting data to Equation 1 (see text).

Temp °C	Rate Constant, k min^{-1}
80	4.1×10^{-5}
100	4.0×10^{-4}
125	1.4×10^{-3}

As is evident from figure 12, the kinetics of the degradation process are clearly non-linear. The magnitude of the rate constant above 100 C bears mentioning in more detail. It is known that polyTHF degrades in air above 90 C. One of the byproducts of this degradation are hydroxy radicals (10). These radicals could react with the delocalized backbone of the polythiophene, thus causing a loss in conductivity. Figure 11 reveals the result of this mechanism. At 125 C, log R_t/R_o after 900 minutes was 1.3 , considerably higher than the 0.2 at 125 C for polypyrrole/toluene sulfonate (see figure 2) Thus, polythiophene/polyTHF although rather stable at room temperature should not be exposed to temperatures above 80 C for extended periods of time.

Section 4: Attempted synthesis of polyfuran multicomponent systems

Polyfuran is the oxygen analog of polythiophene and has been electrochemically synthesized in the form of powders with the ClO_4^- species as the anion (11). It was hoped that utilizing the approach in section 3 for polythiophene/polyTHF multicomponent systems, a polyfuran/polyTHF multicomponent system with improved mechanical intergrity and stability could be synthesized.

Attempts to synthesize the multicomponent were performed in an analogous manner as in section 3. It was not possible, however, to synthesize a macroscopically homogeneous material. The material obtained was a semitransparent film with polyfuran powder interspersed whose conductivity was $<10^{-4}$ (ohm-cm)$^{-1}$. The reasons for this result stem from the fact that the oxidation potential of the furan monomer is 1.5 V vs Ag/Ag$^+$, while THF oxidation potential is 0.65 V vs Ag/Ag$^+$. Thus, under galvanostatic conditions, the oxidation of THF to polyTHF occurs more readily than the oxidation of furan to polyfuran. As bifuran was not available, we could not start with this material (which should have a lower oxidation potential than furan). It was decided that no further attempts would be made to synthesize polyfuran.

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Section 5: Attempted synthesis of polycarbazole

Polycarbazole, a heterocylic polymer, as recently synthesized by Wellinghoff (12) was reported to be stable at room temperature for an indefinite period of time. The doped polymer was made as the result of the polymerization of the carbazole monomer by liquid I_2. At the present time, the only known dopant for polycarbazole is iodine. It was believed that the use of stronger electron transfer agents such as nitrosyl hexafluorophosphate (NOPF$_6$) would lead to higher conductivities. Additionaly, since the polycarbazole/I_2 complexes lose iodine at higher temperatures (12), it was anticipated that the PF$_6^-$ anion would lead to higher thermal stability. The concept was to simultaneously polymerize and dope the carbazole monomer in a nitrosyl hexafluorophosphate/nitromethane solution.

Attempts to synthesize the doped polycarbazole by the published procedure were not very successful. A one to one mixture of iodine and carbazole were heated in a beaker (in laboratory air) until the mixture melted. The mixture was stirred with a stirring rod in order to insure a homogeneous solution of monomer in liquid iodine. An evolution of gas was observed and the mixture became more viscous. The mixture could be coated on a glass slide and when cooled, a brittle film was obtained. The conductivity of the film was $<10^{-3}$ (ohm-cm)$^{-1}$. All attempts to improve this synthesis and reach levels of conductivity comparable to those reported previously were unsuccessful and it was decided not to continue the synthetic effort.

Section 6: Incorporation of Metal Containing Anions into Polypyrrole

The dielectric and loss properties of a conducting polymer should in principle not just depend on the dopant species and dopant polymer interaction but depend as well on the total properties of the polymer dopant system. Thus, the nature of the dopant distribution and the organisation of the polymer chains and overall morphology will ultimately dictate the dielectric and loss properties of the conducting polymer system.

Previous research had demonstrated that IrCl$_6^{2-}$ doped polyacetylene had a dielectric constant of 10^3 while that of I_2 doped polyacetylene was 10^2 (13). This was attributed to the fact that due to the large size of the IrCl$_6^{2-}$ species, aggregation of dopant molecules occur, such that there are conducting regions separated by a very thin interphase of insulating material. Thus, polarization of these conducting islands as a result of an applied field gives rise to an extremely large polarization vector

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for the whole medium. Eventually conduction occurs by charging limited tunneling between these islands. The result of this polarization mechanism is the large dielectric constant observed in $IrCl_6^{2-}$ doped polyacetylene. Thus, it was felt that the dopant species might affect the dielectric properties of polypyrrole and therefore incorporation of metal containing anions would also be attempted.

The first attempts centered upon the concept of direct incorporatation as a result of electrochemical polymerization. Normally pyrrole is electrochemically polymerized using an electrolyte such as lithium perchlorate. The perchlorate anions are then incorporated into the polymer during the polymerization. If a salt such as tetrabutylammonium hexachloroiridate (IV) is used as the supporting electrolyte in an electrochemical cell, then the hexachloroiridate anion would be incorporated during the polymerization of pyrrole. It was not possible, however, to polymerize pyrrole in the presence of hexachloroiridate. Although a cyclic voltammetry experiment revealed that the pyrrole monomer does oxidize in the presence of the hexachloroiridate species, a polymer film is not formed. The solution at the working electrode changes from a deep red color at the beginning of the oxidation of pyrrole (the dark red color is due to the $IrCl_6^{2-}$ species) to a yellow colored solution. The yellow color could be due to either the $IrCl_6^{3-}$ species or pyyrole oligomers. In any case the pyrrole cation radical species was not able to form a polymer film at the electrode surface.

Another method by which a metal containing anion can be incorporated is to first polymerize pyrrole in the usual manner and then undope it chemically with treatment by base. Utilizing this approach we demonstrated that 100 micron thick polypyyrole films could be undoped with base and then redoped with nitromethane solutions of $FeCl_3$. In table 5 we show the results of this process.
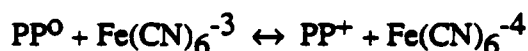
Table 5

Conductivity of Polypyrrole before and after treatment with base followed by doping with $FeCl_3$

Conductivity before Treatment with KOH	Conductivity After Treatment with KOH	Conductivity After Doping with $FeCl_3$
46 $(ohm\text{-}cm)^{-1}$	0.0063 $(ohm\text{-}cm)^{-1}$	0.022 $(ohm\text{-}cm)^{-1}$

Attempts to increase the doping level where unsuccessful.

The conductivity of the iron chloride doped film decreased to 10^{-4} $(ohm\text{-}cm)^{-1}$ in just three days exposure to air at room temperature. Since this behavior is not typical of doped polypyrrole, an

interaction between the dopant and the polymer backbone causing this degradation must be present. A subsequent interaction with oxygen and water is also postulated. Confirmation of the first hypothesis comes as a result of recent electron spin resonance measurements on iron chloride doped polypyrrole. The investigators reported that when polypyyrole is doped with an iron species such as $Fe(CN)_6^{-4}$ a reversible electronic interaction between the dopant and the polymer backbone occurs resulting in the formation of the $Fe(CN)_6^{-3}$ species (14). This may be represented by the following chemical reaction:

$$PP^O + Fe(CN)_6^{-3} \leftrightarrow PP^+ + Fe(CN)_6^{-4}$$

The implication of this reaction is that even when polypyrrole is doped with an iron containing species, there is a tendency for the reverse reaction to spontaneously occur, resulting in undoped polypyrrole. Depending on the degree of reversibility, the polypyrrole will be either partially undoped or completely undoped. For this reason, the lower conductivity obtained when polypyrrole was doped with the iron chloride species is easily understood. The poor environmental stability of the iron chloride doped polypyrrole is due to the presence of the neutral polypyrrole. Neutral polypyrrole reacts with both air and water and is therefore not environmentally stable. Because there is more neutral polypyrrole present than in polypyrrole doped with other species, the environmental stability of the doped polymer is less than usually found for doped polypyrrole.

Section 7: Dielectric Measurements

Measurements of the dielectric properties of polypyrrole as a function of dopant anion were performed over a broad frequency range. The following measurements were performed:

50-75 GHz: waveguide
95 GHz: open range RCS
1-20 GHz: coaxial wave guide
5-18 GHz: waveguide

The 95 GHz and 8.2-18 GHz measurements were performed at Boeing Aerospace while the 50-75 GHz and 1-20 GHz measurements were performed at General Dynamics-Convair Division. With the exception of the 95 GHz measurement the following polypyrrole samples were measured:

Polypyrrole/Toluene Sulfonate
Polypyrrole/Tetrafluoroborate

Polypyrrole/Trifluoromethyl sulfonate

Polypyrrole/Toluene Sulfonate Multicomponent system

Polythiophene/PolyTHF Multicomponent system

At 95 GHz the polypyrrole/toluene sulfonate was the only sample measured. The reason for this was that since this measurement required large amounts of sample and the measurements at lower frequencies did not indicate that the anion had an effect on the dielectric properties, it was decided only to investigate the toluene sulfonate system.

50-75 GHz measurements

These measurements were performed in a wave guide set-up and the return loss and insertion loss was measured directly. The "return loss" is the amount of signal that is not reflected back, this includes that part of the signal that is transmitted into and through the sample. An ideal metal has zero return loss. The insertion loss refers to of the signal that is not returned , the amount that is not transmitted through the sample.

The samples were 0.275 inch diameter disks cut from a single sheet of film, thus the thicknesses were 3-4 mil (0.08-1 micron). The samples were positioned in the wave guide and three measurements were taken over each of the three bands and the average losses were determined and plotted. Because of problems in obtaining an accurate calibration of the second band (54-64 GHz), the losses in this region are not considered accurate, the losses should be extrapolated over this range from the endpoints of the first and third bands. Figures 13-17 represent the return loss for the multicomponent polypyrrole/toluene sulfonate, polypyrrole/toluene sulfonate, polypyrrole tetrafluoroborate, polypyrrole/trifluoromethyl sulfonate, and polythiophene multicomponent system, respectively. As is evident from examination of these figures is that the return losses for the polypyrrole samples are indicative of the conductivities of these materials being weak metals, i.e the return losses were nearly that of an ideal metal. The behavior of the polythiophene/polyTHF multicomponent system is indicative of the lower conductivity of this sample. The conductivities of the materials are listed below in Table 6.

Figure 13: Return loss for multicomponent polypyrrole/toluene sulfonate at 50-75 GHz. Return loss is defined as the amount of signal not reflected back, including that part which is transmitted into and through the sample. Ideal metal has zero return loss.
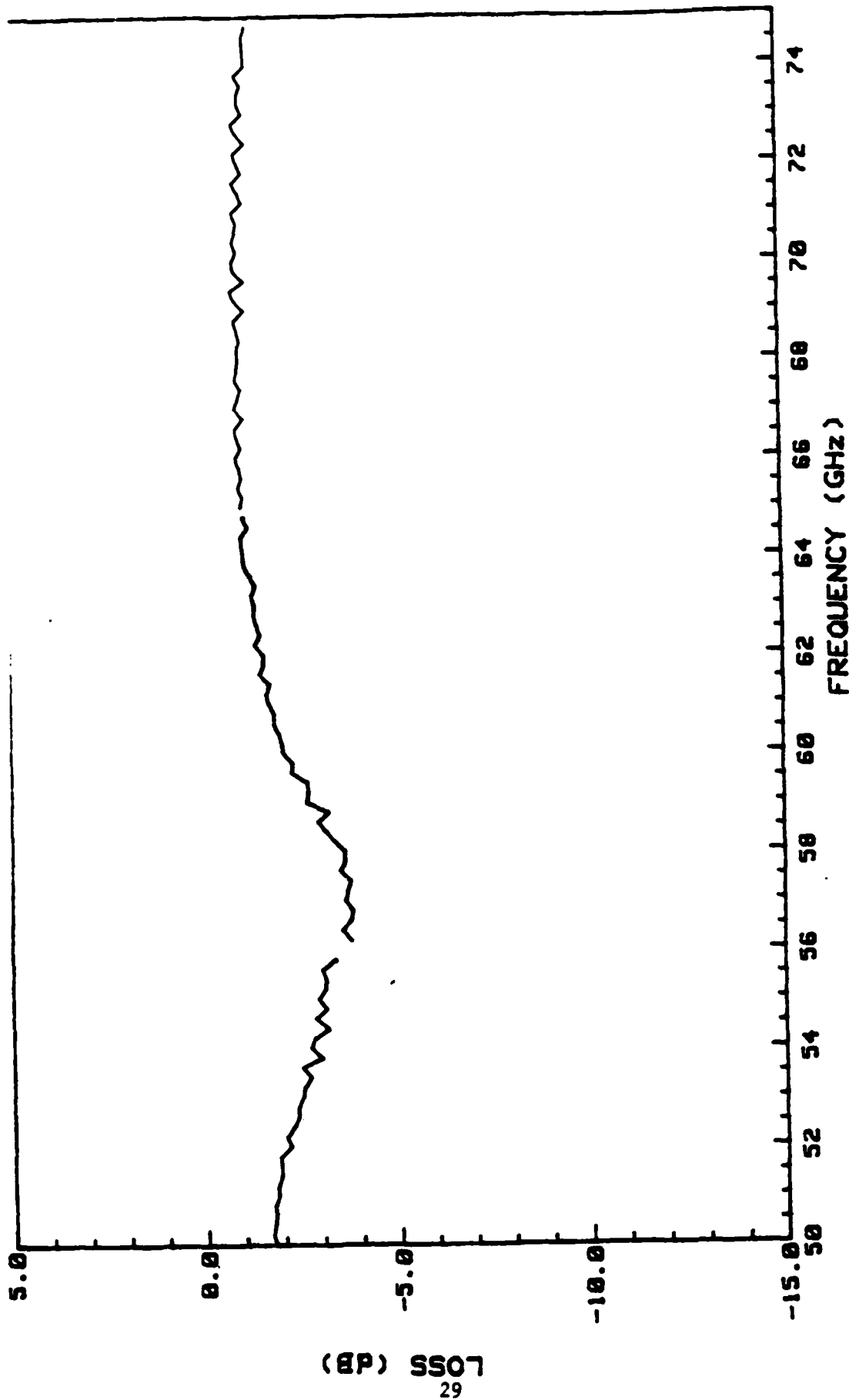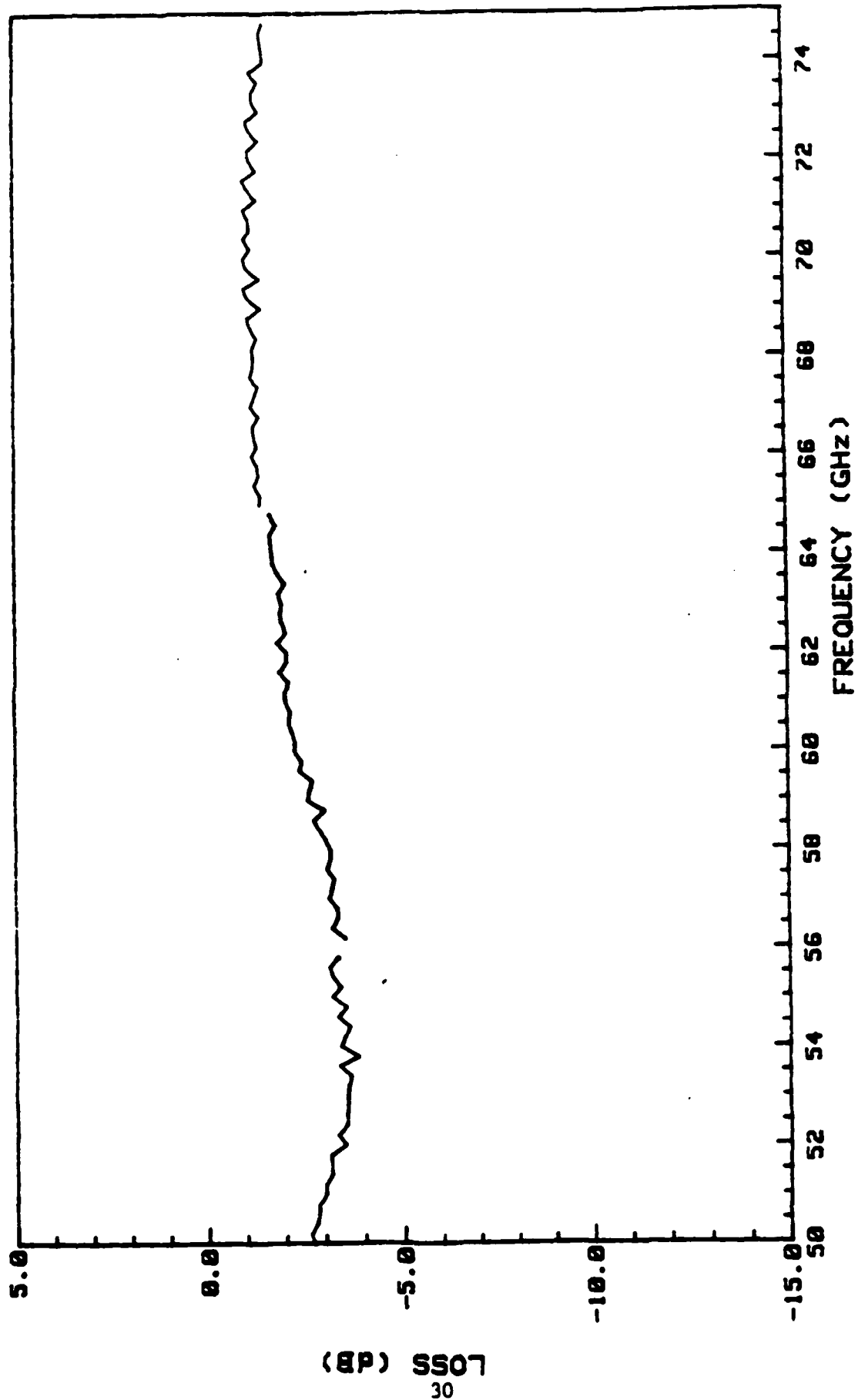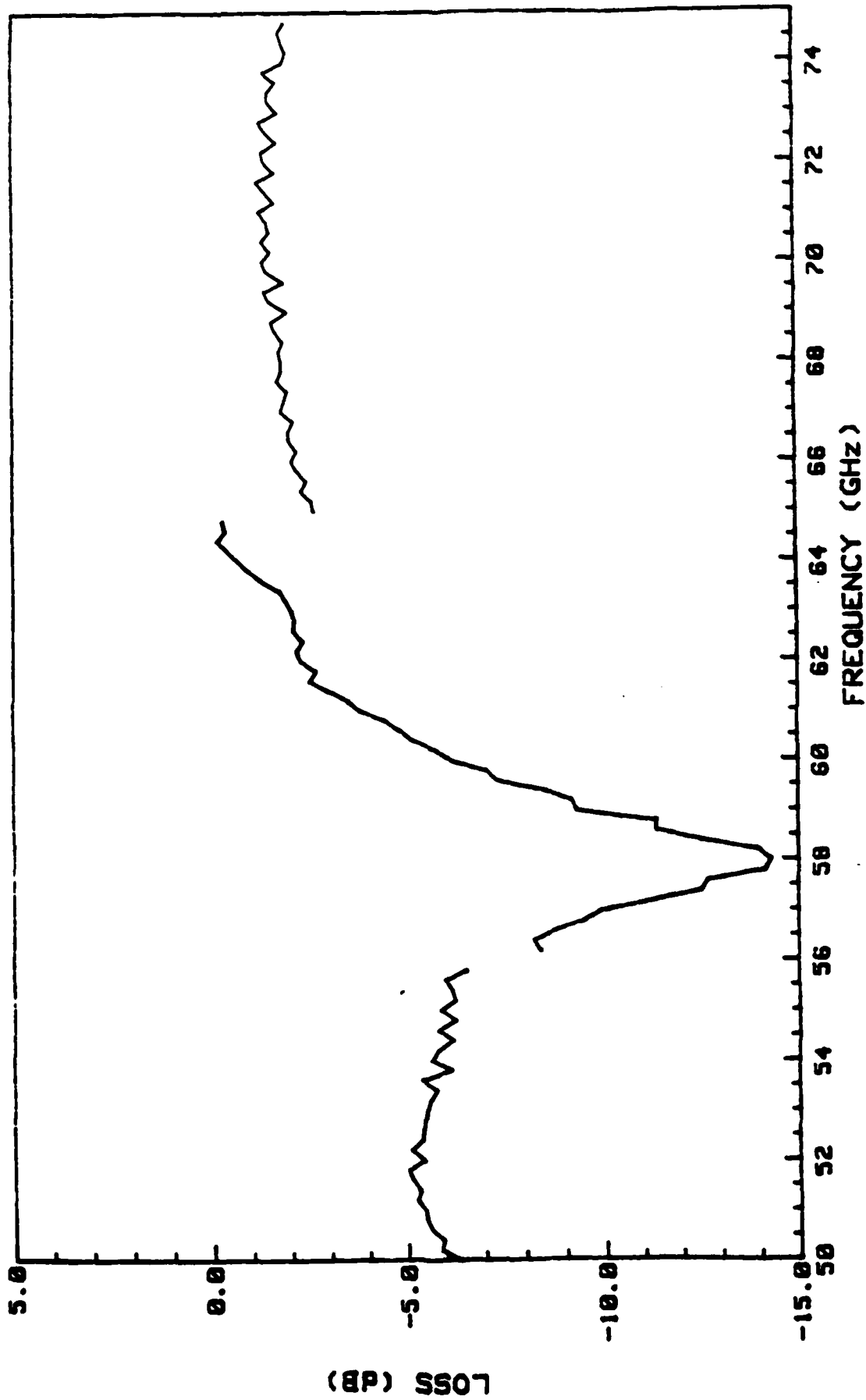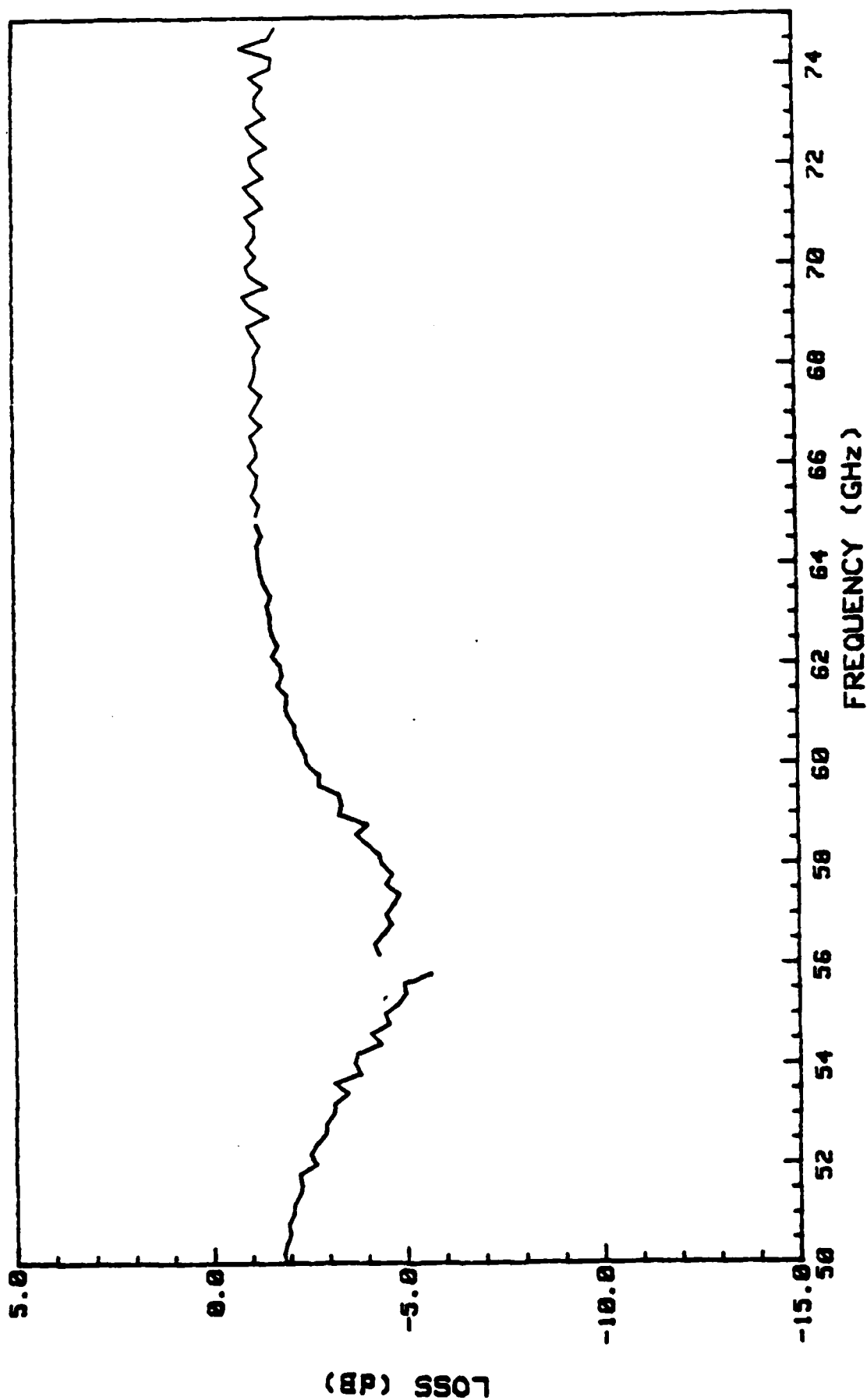
29

Figure 14: Return loss for polypyrrole/toluene sulfonate at 50-75 GHz. Return loss is defined as the amount of signal not reflected back, including that part which is transmitted into and through the sample. Ideal metal has zero return loss.
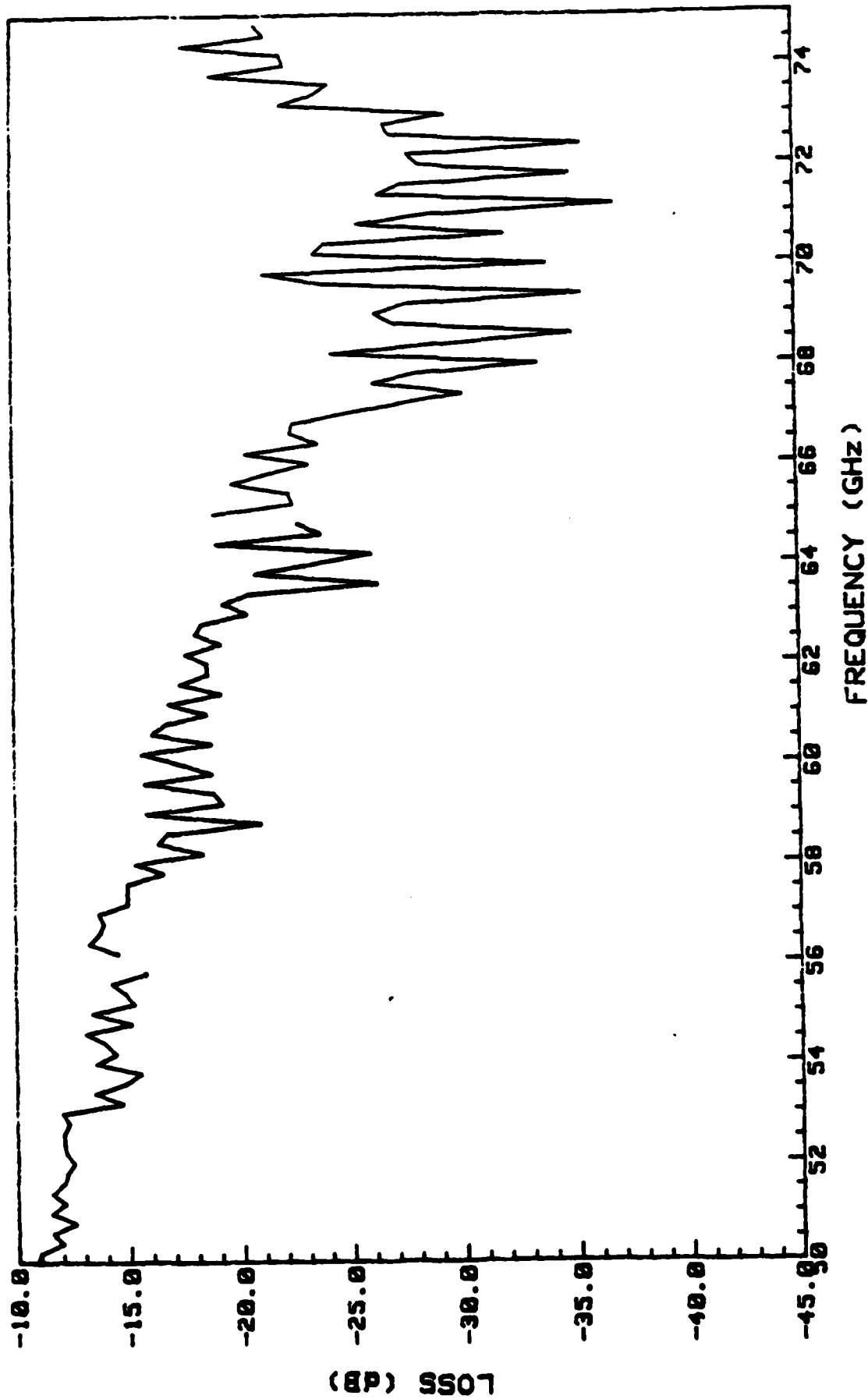
30

Figure 15: Return loss for polypyrrole/tetrafluoroborate at 50-75 GHz. Return loss is defined as the amount of signal not reflected back, including that part which is transmitted into and through the sample. Ideal metal has zero return loss.

Figure 16: Return loss for polypyrrole/trifluoromethyl sulfonate at 50-75 GHz. Return loss is defined as the amount of signal not reflected back, including that part which is transmitted into and through the sample. Ideal metal has zero return loss.

Figure 17: Return loss for polythiophene multicomponent system at 50-75 GHz. Return loss is defined as the amount of signal not reflected back, including that part which is transmitted into and through the sample. Ideal metal has zero return loss.

Table 6

Conductivities of Samples measured at 50-75 GHz

Sample	Conductivity, $(\text{ohm-cm})^{-1}$
Multicomponent pP/PTS	120
pP/PTS	131
pP/BF$_4$	178
pP/CF$_3$SO$_3$	131
polythiophene/PolyTHF/ClO$_4$	0.01

Figures 18-22 represent the correponding insertion losses. As is evident from this data, the polypyrrole samples are absorbers in this frequency range, whereas the polythiophene sample does not absorb but rather transmits the signal through the sample. As is apparent from this data, the loss characteristics of these materials appear to be derived from the conductivity levels of the samples. There did not appear to be any effect of the anion on the measured losses.

These samples were also measured at 8-18 GHz as single sheets in a wave guide. Microwave conductivity measurements were made by placing the sample in the measurement arm of a waveguide bridge (see figure 23) at the transmission station. Two values of complex surface impedance, R +jX (ohm/sq) were computed: one from the measured complex reflection coefficient and the other from the complex transmission coefficient. Measurements covering the frequency range, 8.2 GHz < f < 12.4 GHz were made in an X-band bridge; those covering the range 12.4 < f < 18.0 GHz were made in a K_u band bridge. K_u band measurements were made for two orthogonal (with respect to the electric field) sample orientations (designated L and W). Because of the high conductivity of the samples, neither the frequency dependences nor the average values indicated for R and X are considered to be particularly accurate. The results are summarized in table 7. From these values of the microwave impedance it is possible to calculate the imaginary component of the dielectric constant (ε'') from the equation

$$\varepsilon'' = \sigma/0.055f$$

where f= frequency in GHz, and σ is the conductivity in $(\text{ohm-m})^{-1}$. These values are tabulated in table 8.

As is evident from examination of the data, there does not appear to be an effect of dopant anion on

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Figure 18: Insertion loss for polypyrrole toluene sulfonate multicomponent system. Insertion loss refers to of the signal that is not returned, the amount that is not transmitted through the sample.
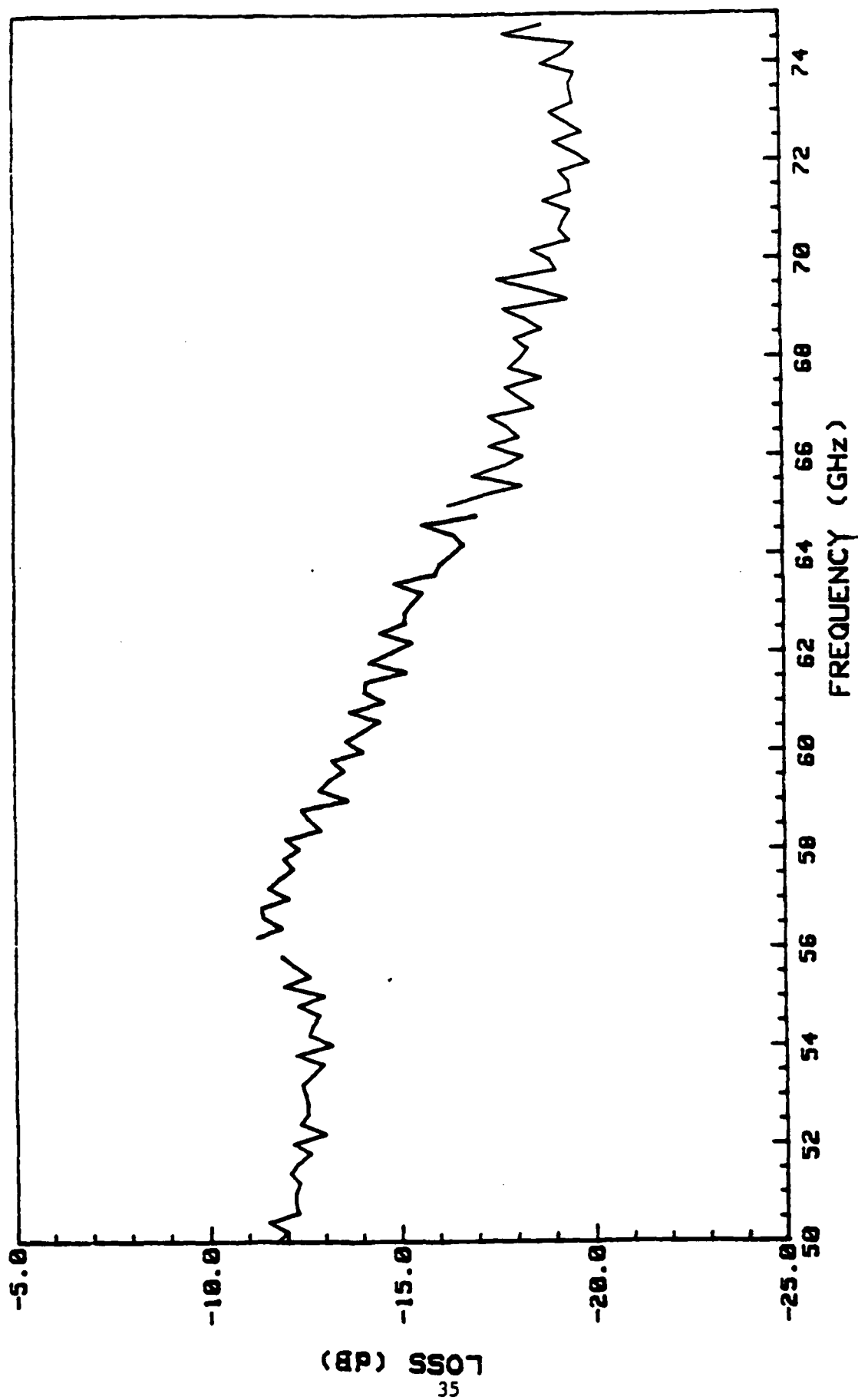
Figure 19: Insertion loss for polypyrrole/toluene sulfonate. Insertion loss refers to of the signal that is not returned, the amount that is not transmitted through the sample.
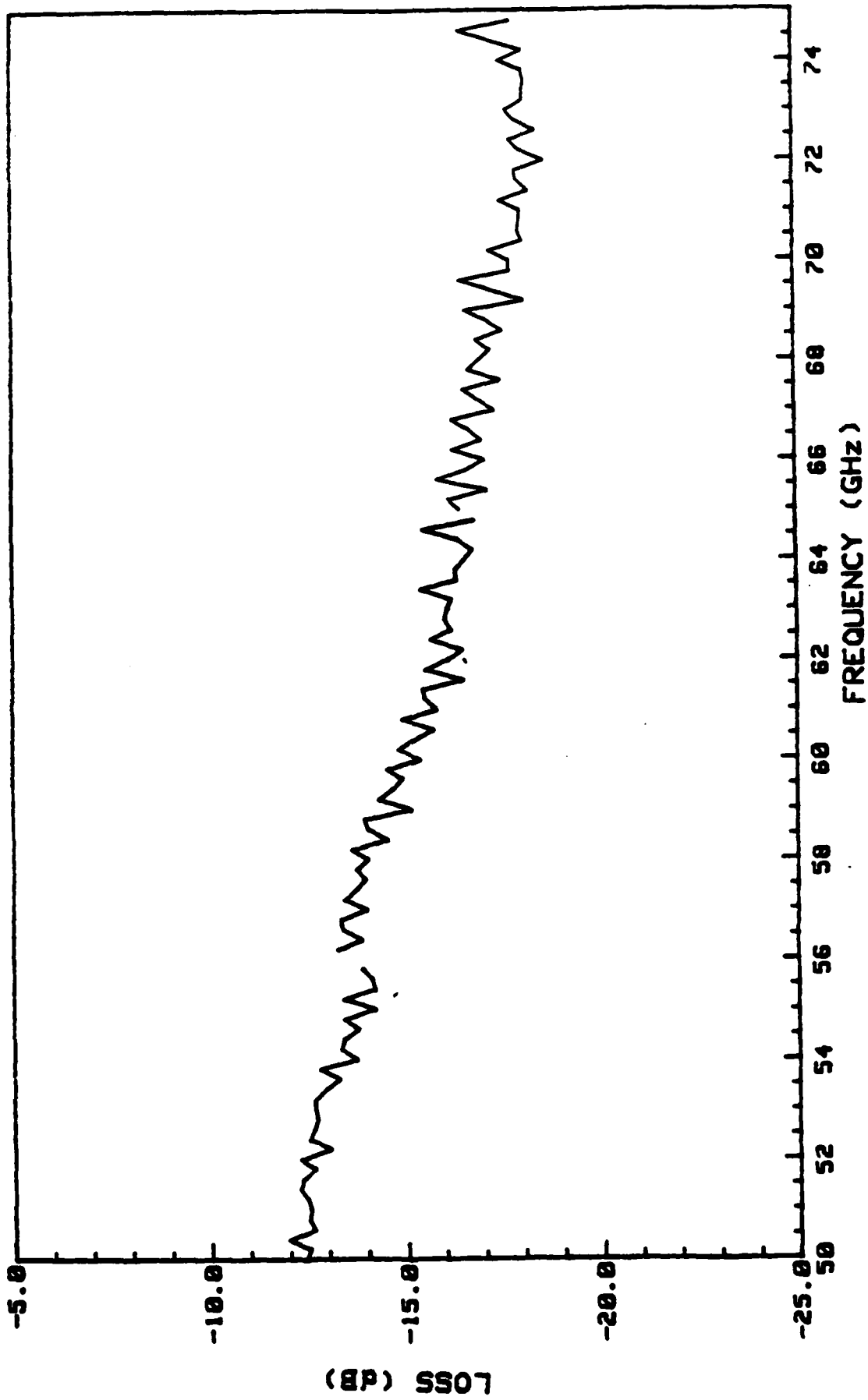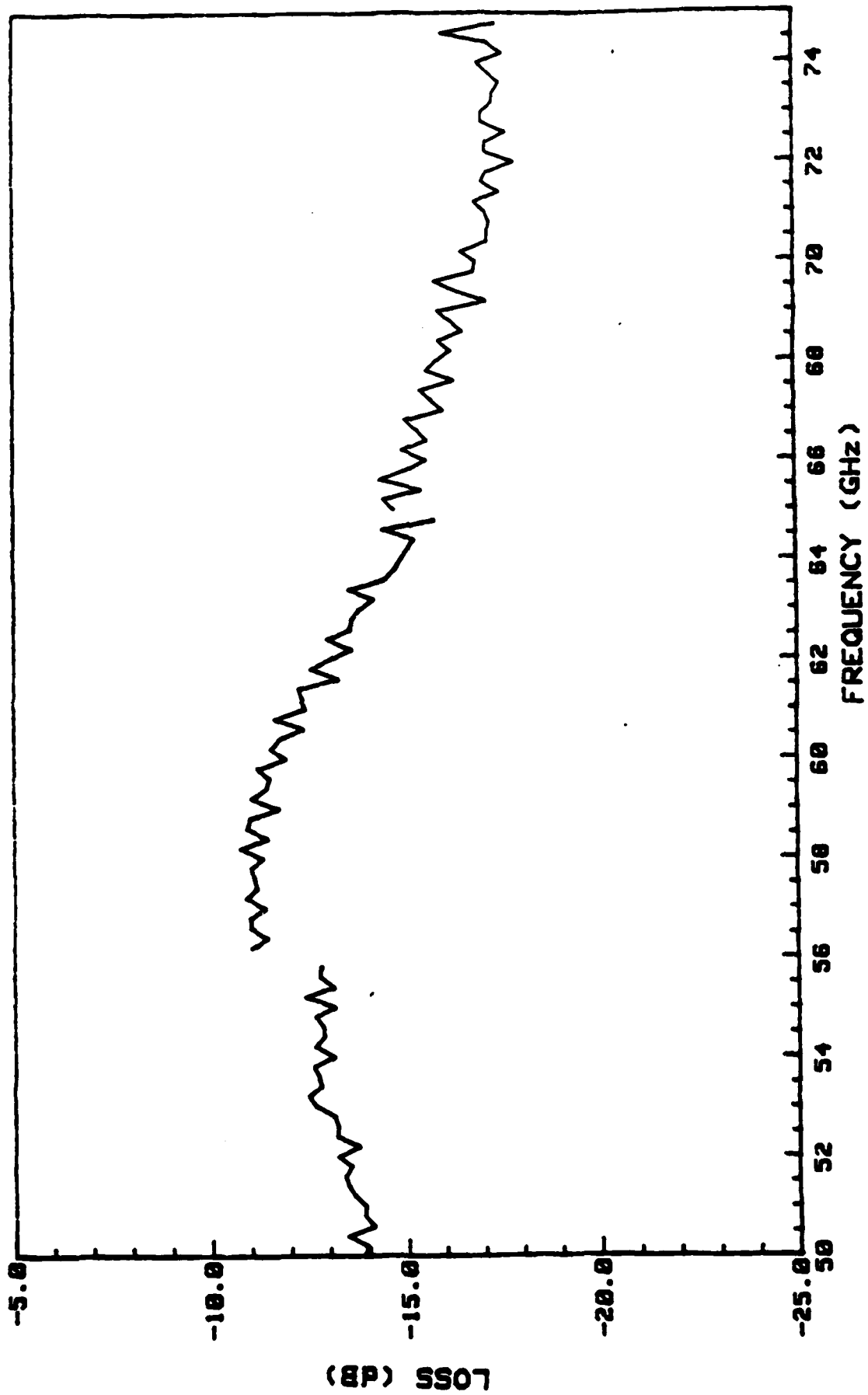
Figure 20: Insertion loss for polypyrrole/tetrafluoroborate. Insertion loss refers to of the signal that is not returned, the amount that is not transmitted through the sample.

Figure 21: Insertion loss for polypyrrole/trifluoromethyl sulfonate. Insertion loss refers to of the signal that is not returned, the amount that is not transmitted through the sample.
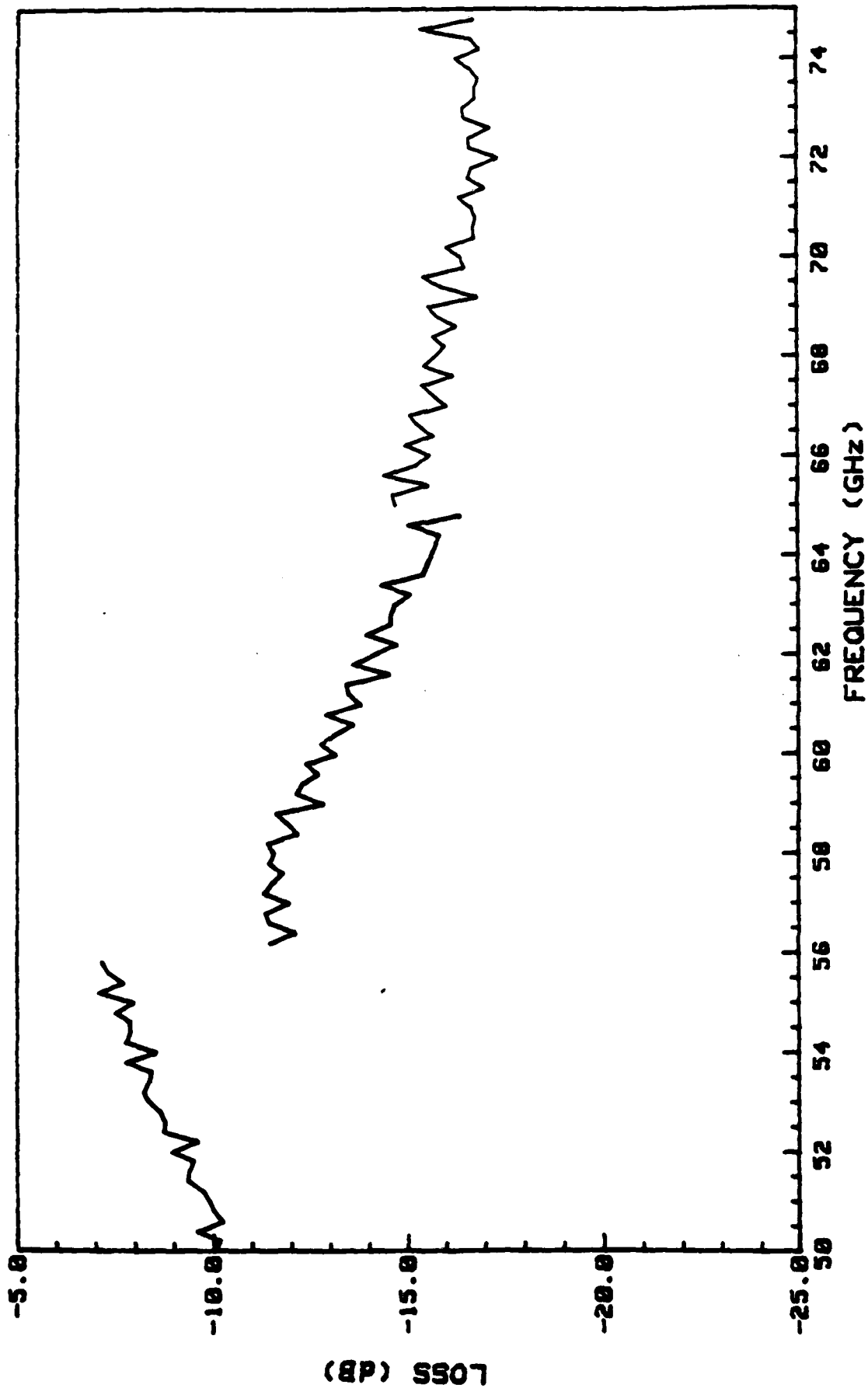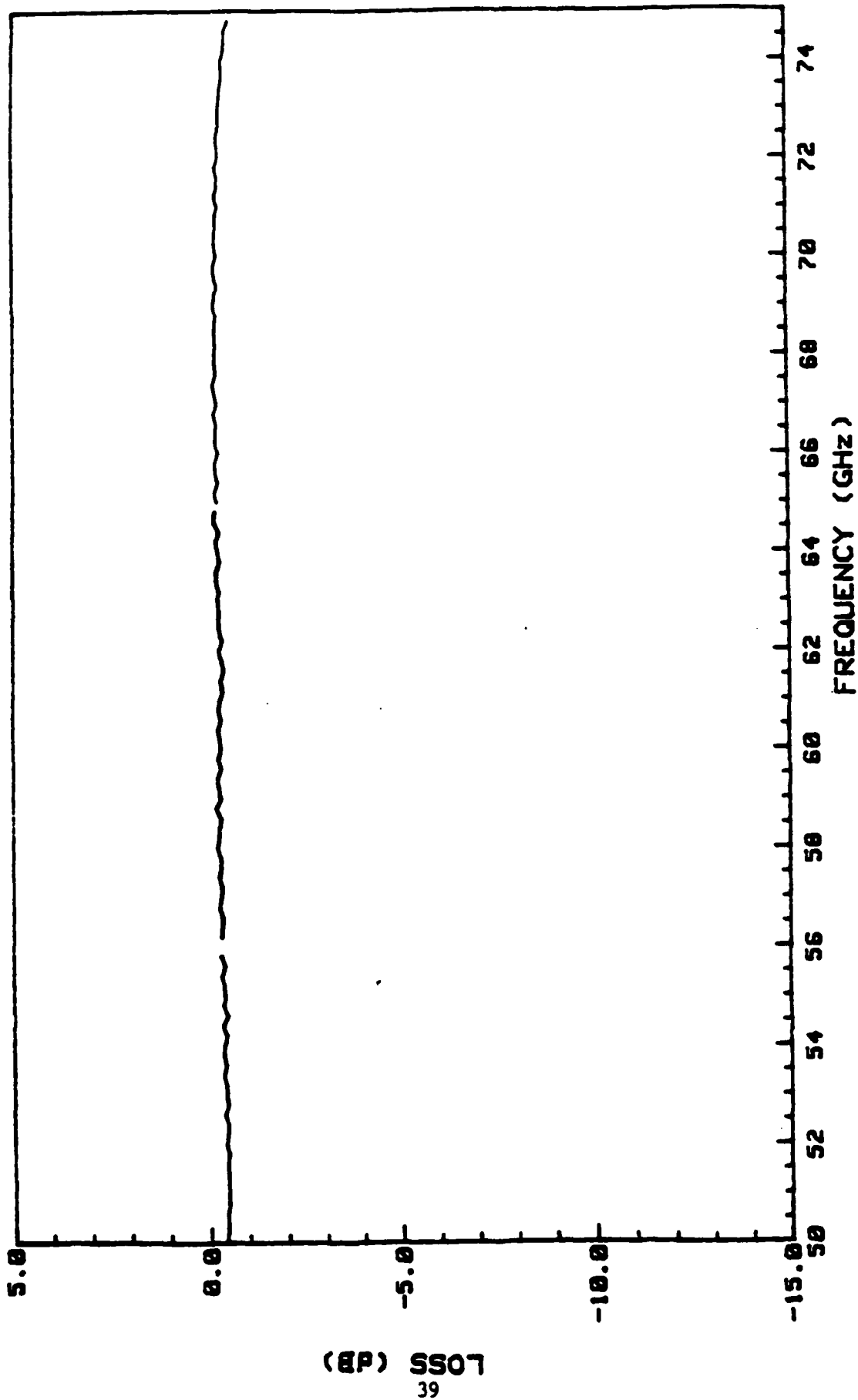
Figure 22: Insertion loss for polythiophene/polyTHF multicomponent system. Insertion loss refers to of the signal that is not returned, the amount that is not transmitted through the sample.
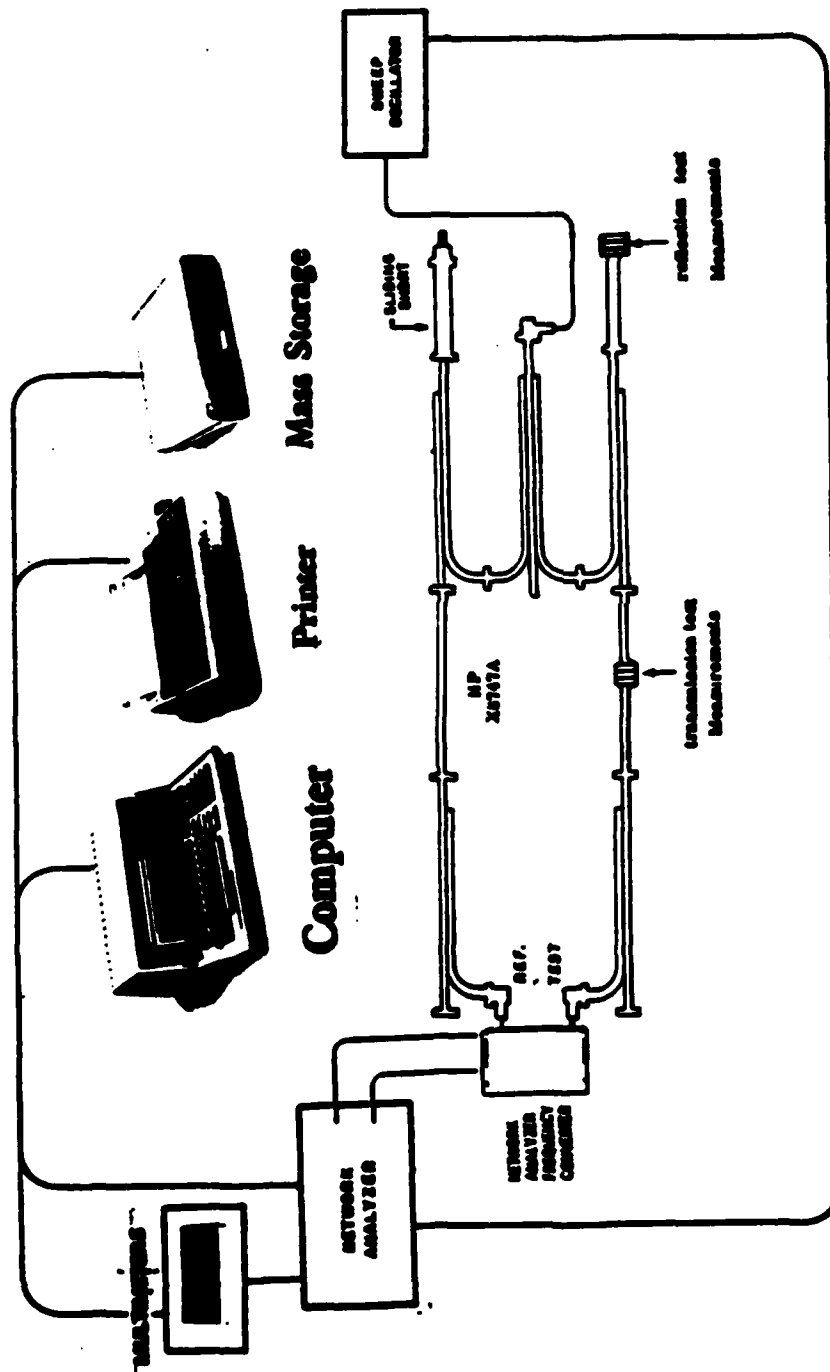
Figure 23: Schematic of wave guide system used for measurements at 8-18 GHz.

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Table 7

Summary of Microwave Impedance Measurements on Polypyrrole/toluene sulfonate, polypyrrole/trifluoromethyl sulfonate, and polypyrrole tetrafluoroborate

| | Microwave Impedance (Ω/Ω) | | | | DC Resistivity (Ω/Ω) | | Bulk Conductivity (U/cm) | | |
| | Reflection | | Transmission | | Probe 1 | Probe 2 | σ_1 | σ_2 | σ_0(c) |
	R	X	R	X					
polypyrrole/toluene sulfonate (a)	3.1	-2.5	2.4	-1.8					
W(b)	3.6	2.6	1.4	-2.0					
L(b)	3.3	1.5	1.2	-2.0	0.55	0.62	178.9	158.8	40
polypyrrole/trifluoromethyl sulfonate (a)	3.1	6.4	3.8	-1.6					
W(b)	3.8	-.5	2.8	-2.2					
L(b)	3.7	.7	2.6	2.5	0.9	0.64	136.7	146.5	52
polypyrrole/tetrafluoroborate (a)	3.7	7.5	2.0	-1.4					
W(b)	4.4	2.5	.7	1.4					
L(b)	5.0	-1.6	.7	-1.4	0.3	0.31	410.0	396.9	50

(a) average of resistivities measured at 200 MHz intervals across X-band.

(b) average of resistivities measured at 200 MHz intervals across Ku band, in orthogonal (L&W) directions.

(c) value supplied with samples.

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Table 8

Calculated Values of E" from the microwave impedance measurements (see Table 7)

Sample	*Microwave Impedance $(\Omega\text{-m})^{-1}$				E"			
	10 GHz		18 GHz**		10 GHz		18 GHz**	
	Reflection	Transmission	Reflection	Transmission	Reflection	Transmission	Reflection	Transmission
Polypyrrole/ Toluene Sulfonate t = 0.010 cm	3175	4166	2903	3238	5675	7451	2884	3217
Polypyrrole/ Trifluoromethyl Sulfonate t = 0.0081 cm	3968	3248	3292	4578	7097	5808	3270	4548
Polypyrrole/ Tetrafluoroborate t = 0.0081 cm	3336	6172	2637	17,636	5966	11,038	2620	17,520

* Microwave Impedance: $(\Omega\text{-m})^{-1} = \dfrac{100}{\Omega/_\square \cdot t}$

** Values at 18 GH_Z represent averages of K_u band, in orthogonal (L&W) directions

the dielectric properties. The dielectric properties appear to be controlled by the bulk conductivity of the sample.

95 GHz measurement

An attempt was made to determine the complex dielectric constant of the polypyrole/toluene sulfonate system from measurements of the reflection coefficient (amplitude) at 95 GHz due to samples of identical composition but different thicknesses. In this measurement, six samples (4 in x 2 in) of varying thicknesses (1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 mil) were glued to square metal places, six wavelengths on a side and a value of the dielectric constant was determined.

The samples supplied were too conductive to permit an accurate measurement. The conductivities of the samples were 30-50 (ohm-cm)$^{-1}$. As typified by data shown in figure 24, returns from the film side of the sample could not be distinguished from those due to the metal side. This result is consistent with the reported conductivities of these samples, which (even at their relatively small thicknesses) renders them essentially opaque and highly reflective. Specifically, the skin depth for materials such as the six samples is on the order of 1 mil, less than or equal to the film thickness. The calculated reflection coefficient for a sample whose thickness is 2.5 mil and conductivity 45 (ohm-cm)$^{-1}$ is only about -1 dB relative to that of the metal plate, in qualitative agreement with the data.

1-20 GHz Measurement

In an effort to determine if the high conductivity of the polypyyrole system could be used to some advantage as a conducting filler in a composite matrix, the dielectric properties of the following polypyrrole samples were measured as composites with a polyurethane in a coaxial waveguide:
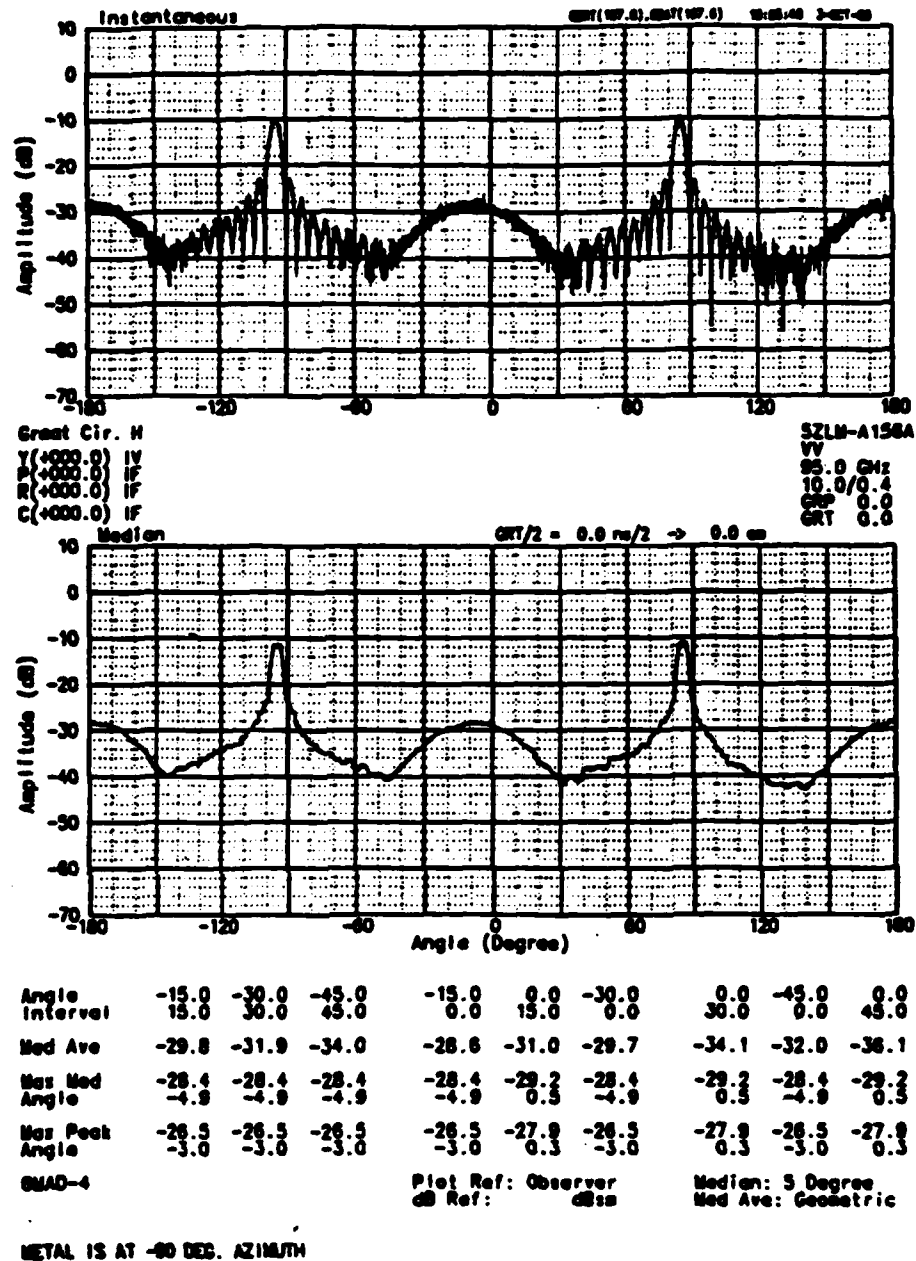
Figure 24: Reflection data at 95 GHz for a 6 λ metal plate coated on one side with a polypyrrole/toluene sulfonate sample.
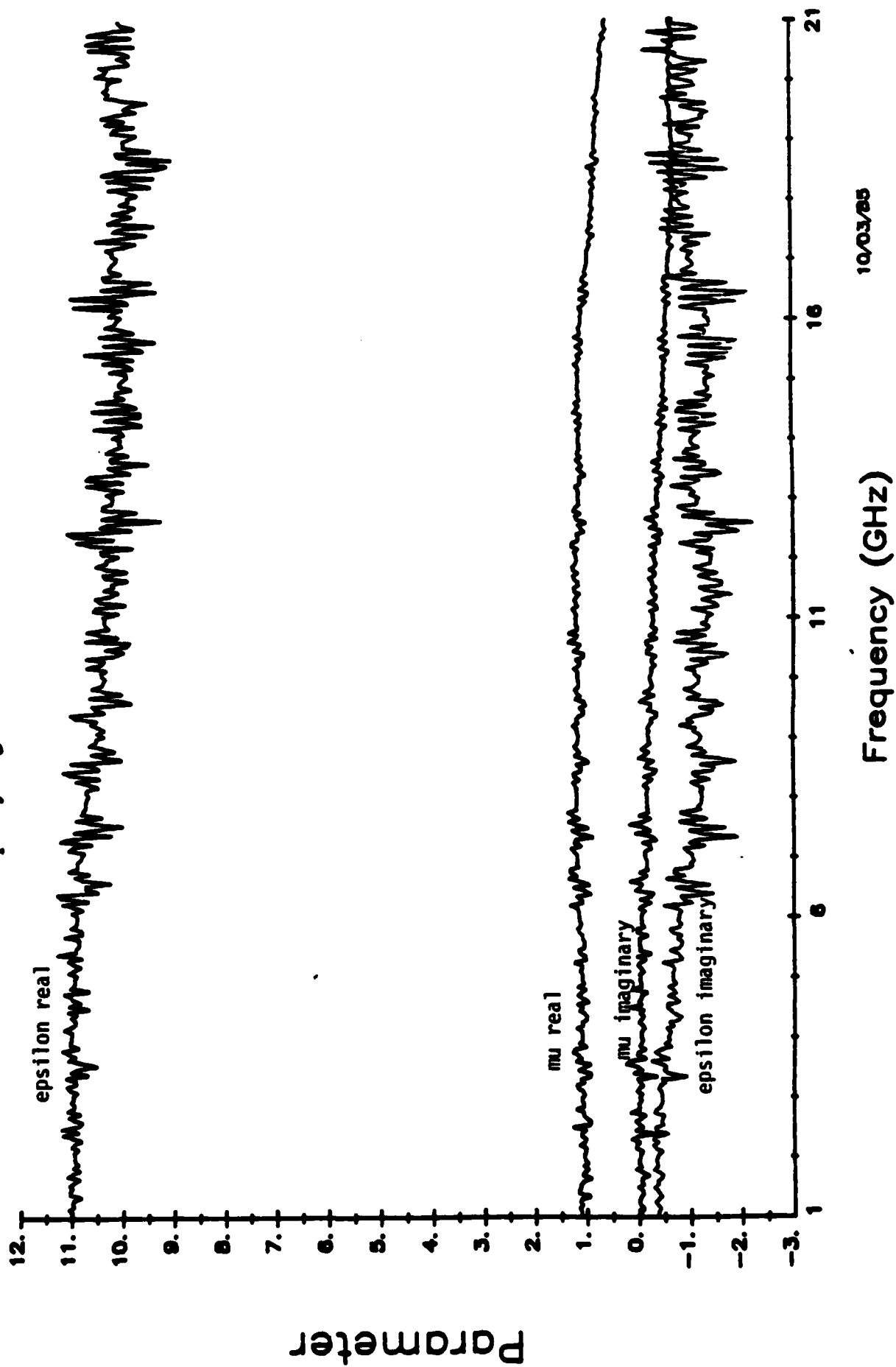
Polypyrrole/PTS Multicomponent

Polypyrrole/PTS

Polypyrrole/BF$_4$

Polypyrrole/CF$_3$SO$_3$

The samples were cut up in a rotating knife blade grinder into a fine powder and mixed with a polyurethane in a 50/50 by weight composition. This mixture was pressed into a toroid of dimensions 0.2751" o.d., 0.1195" i.d., and 0.050" thick. The reflection and transmission coefficients of the composite toroid were obtained over the frequency range of 1-20 GHz and from this data, the real and imaginary components of the permittivity and permeability were calculated. This data is summarized in figures 25-28 for multicomponent polypyrrole/toluene sulfonate, polypyrrole/toluene sulfonate, polypyrrole/tetrafluoroborate, and polypyrrole/trifluoromethyl sulfonate, respectivly. The real and imaginary components of the dielectric constant are reduced considerably from the values obtained as free standing films. The permeability and permittivity data was further analyzed by assuming a metal plate was positioned behind a coating of the composite of the specified thickness. The short circuit return loss from this structure was calculated as a function of frequency. As the data in figures 29-32 indicate there is a large loss.

Figure 25: Dielectric data for multicomponent polypyrrole/toluene sulfonate as a composite over the frequency range 1-20 GHz.

Figure 26: Dielectric data for polypyrrole/toluene sulfonate as a composite over the frequency range 1-20 GHz.

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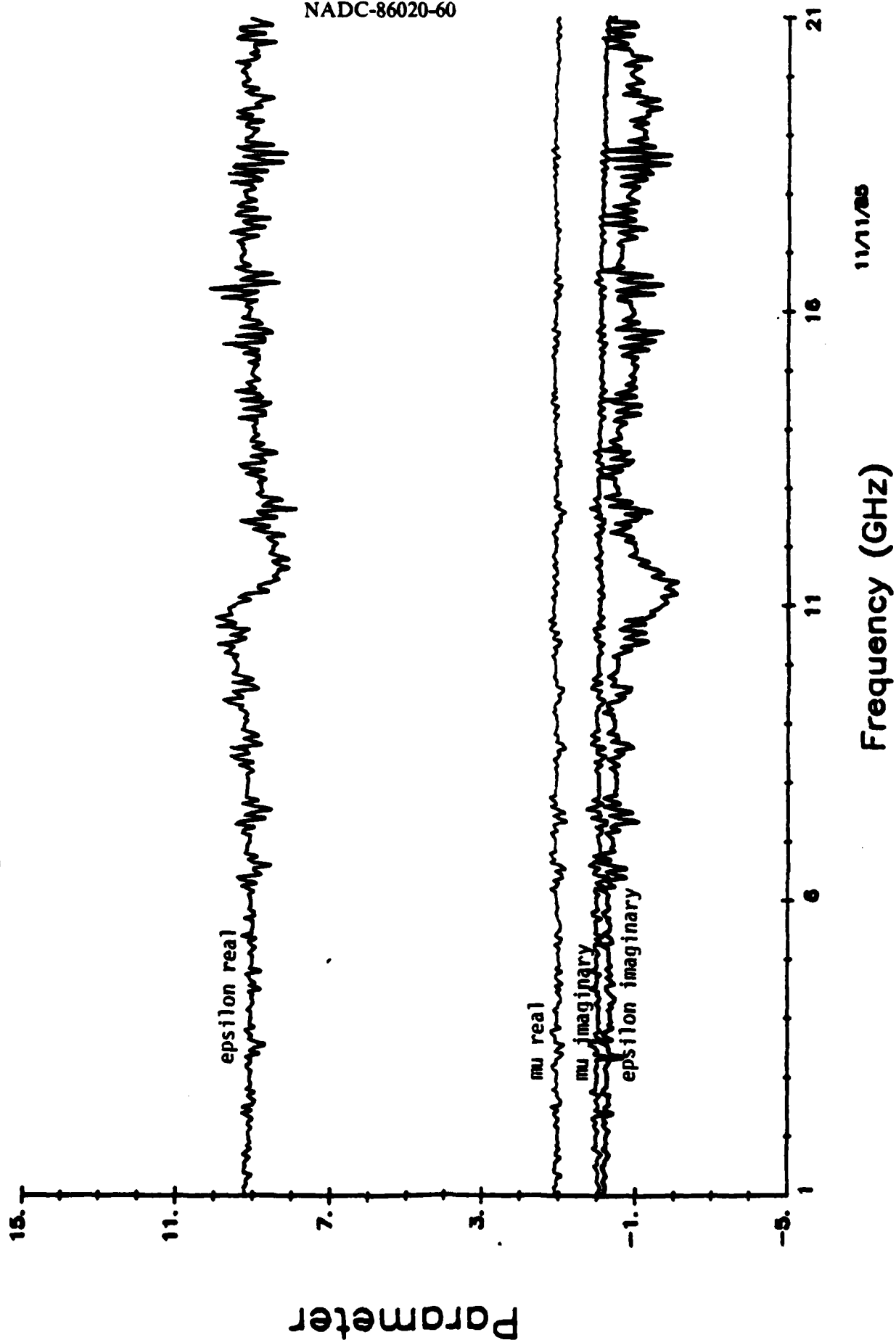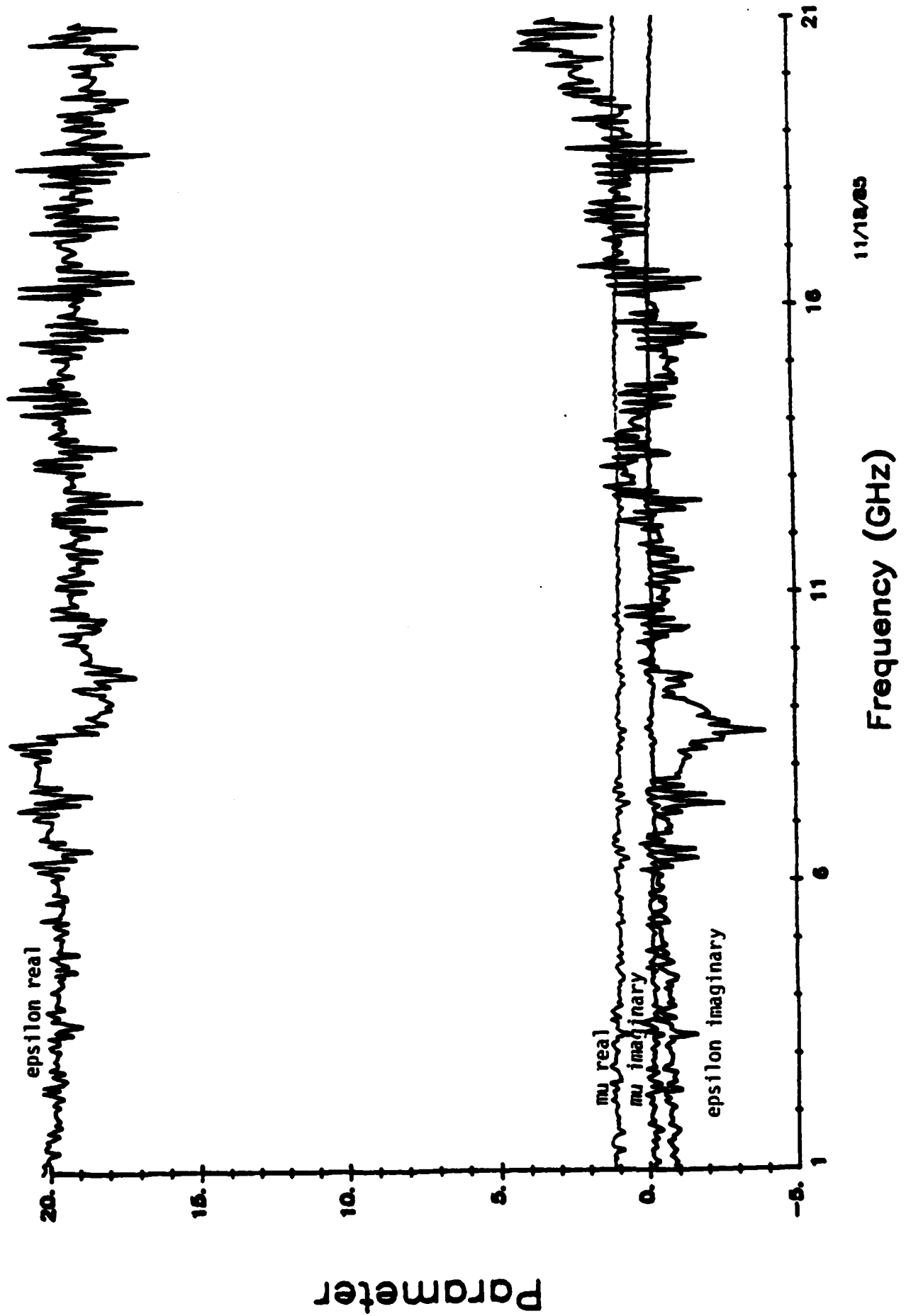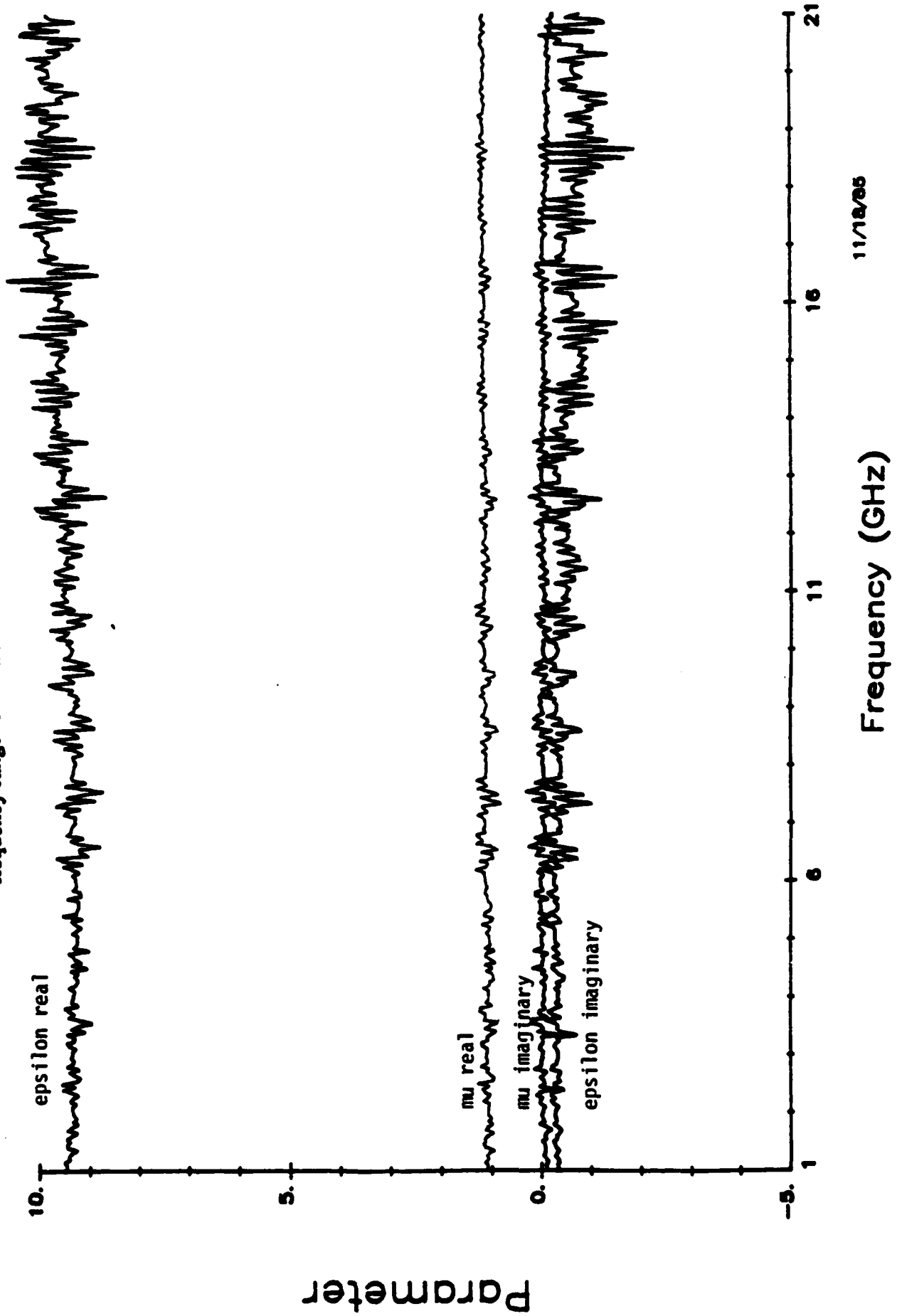
Figure 27: Dielectric data for polypyrrole/tetrafluoroborate as a composite over the frequency range 1-20 GHz.

Figure 28: Dielectric data for polypyrrole/trifluoromethyl sulfonate as a composite over the frequency range 1-20 GHz.

Figure 29: Calculated short circuit return loss for multicomponent polypyrrole/toluene sulfonate as a composite over the frequency range 1-20 GHz.

Figure 30: Calculated short circuit return loss for polypyrrole/toluene sulfonate as a composite over the frequency range 1-20 GHz.
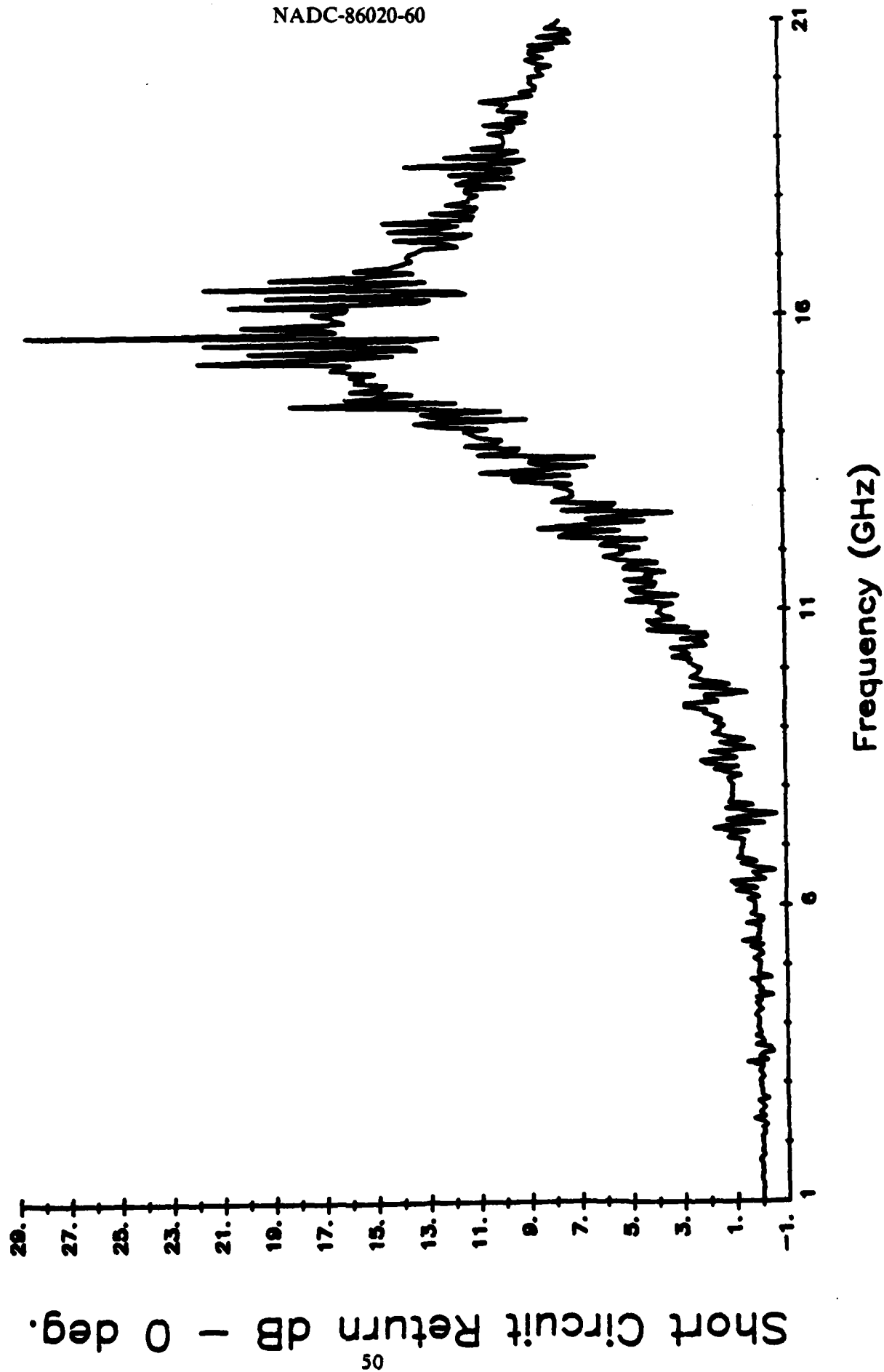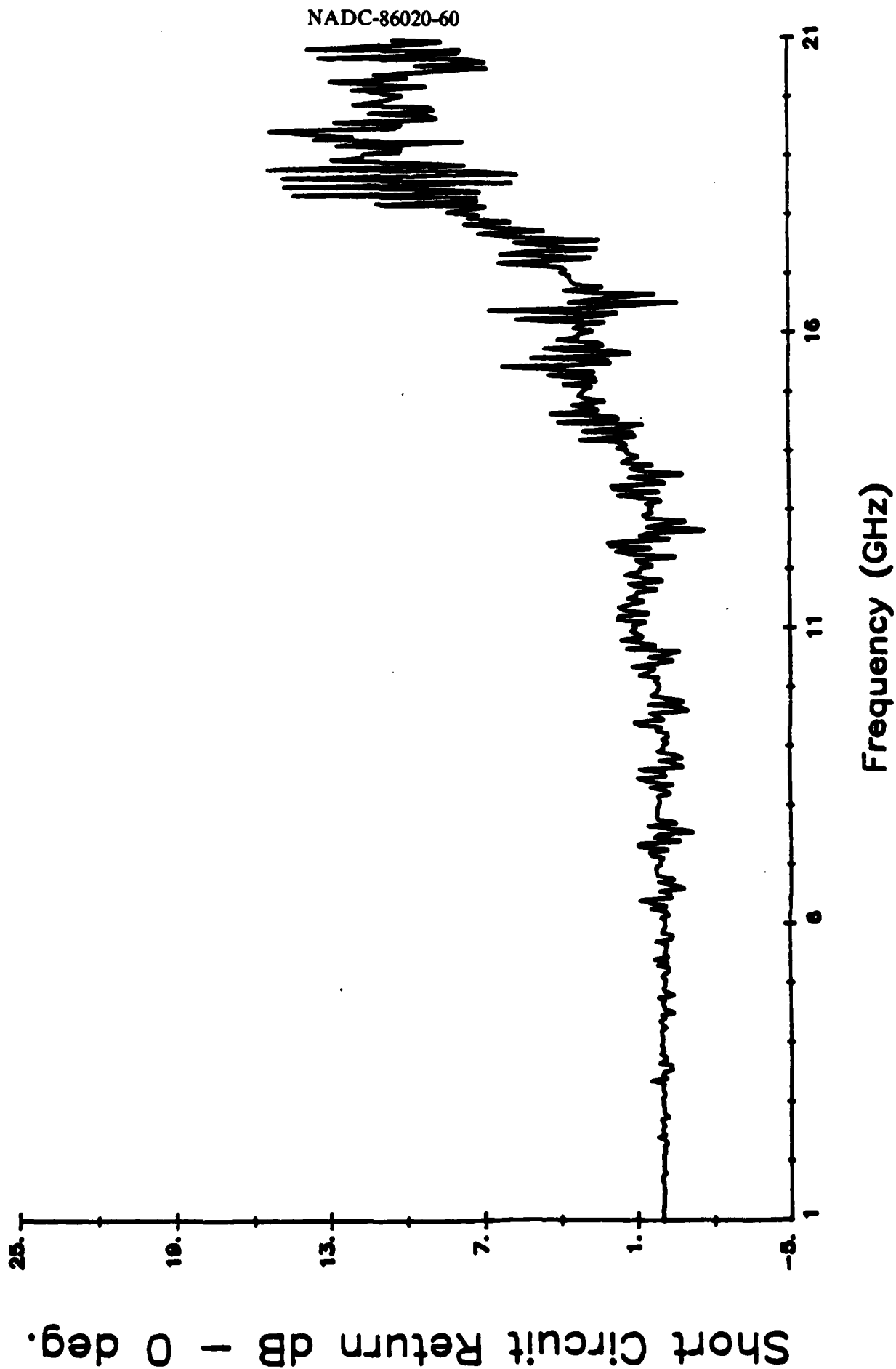
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Figure 31: Calculated short circuit return loss for polypyrrole/tetrafluoroborate as a composite over the frequency range 1-20 GHz.
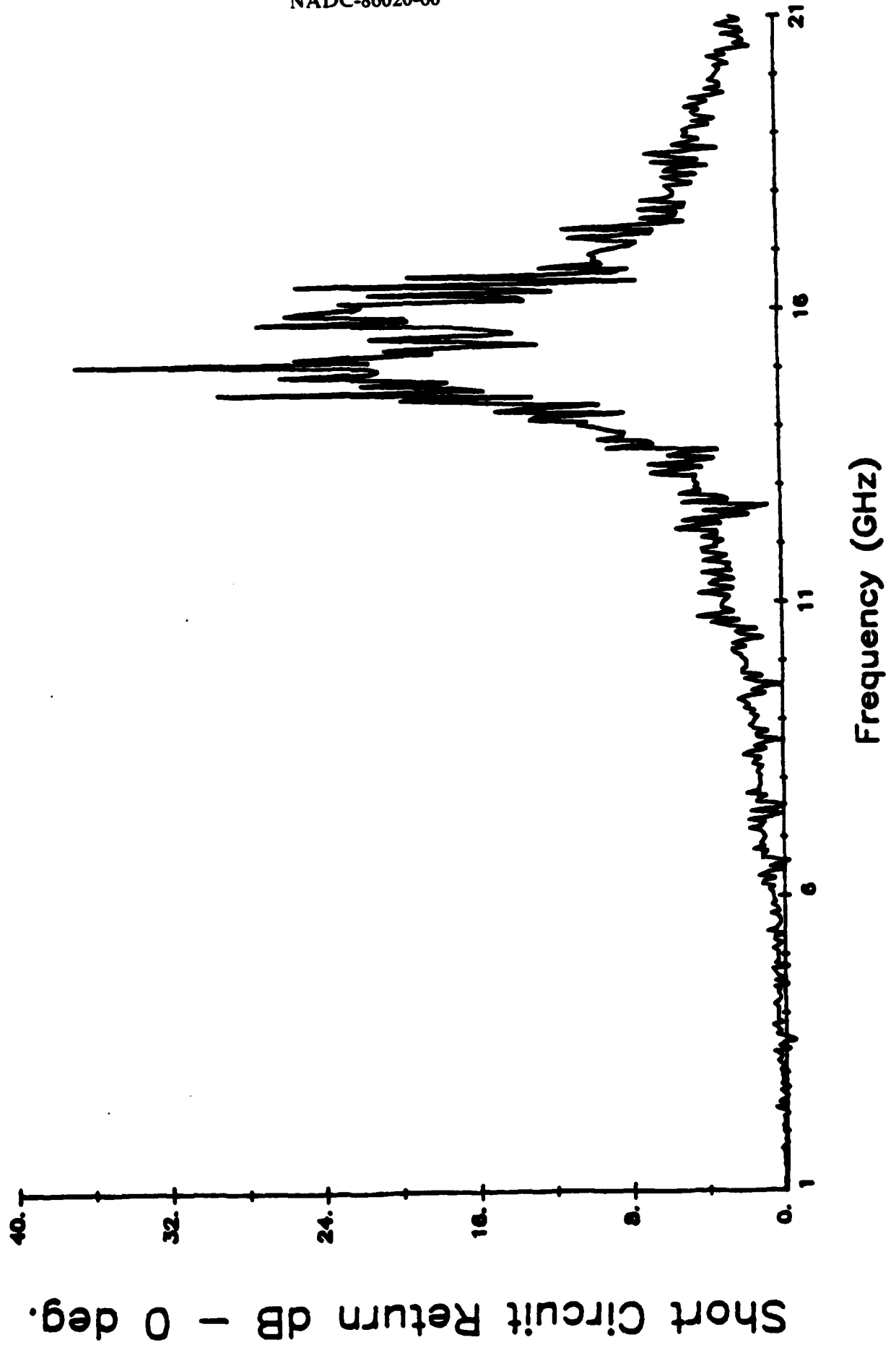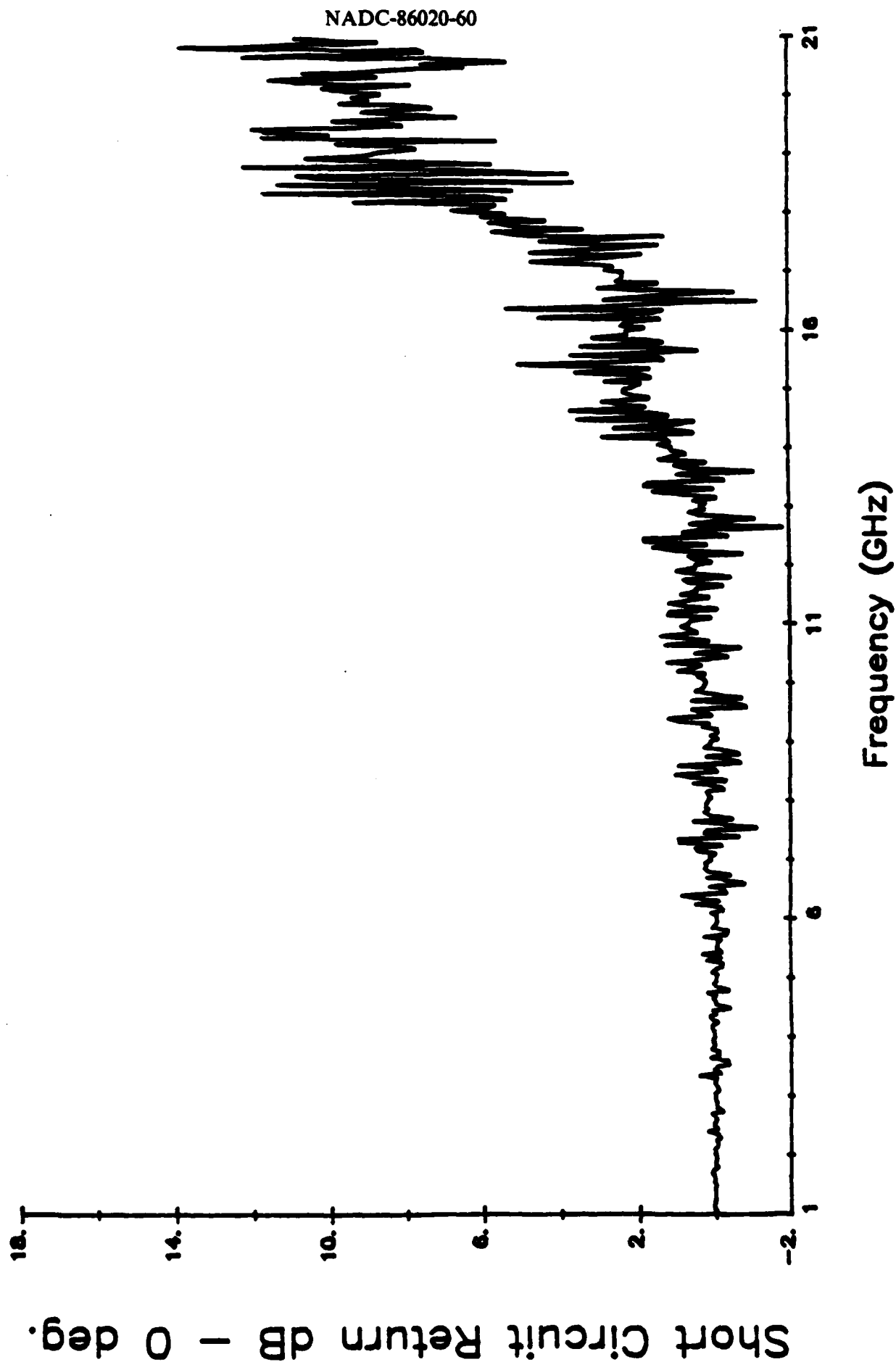
Figure 32: Calculated short circuit return loss for polypyrrole/trifluoromethyl sulfonate as a composite over the frequency range 1-20 GHz.

Section 8: Recommendations

In order to be able to tailor the electrical and mechanical properties of conducting polymer systems over a broad range and maintain environmental and thermal stability, further investigations into the synthetic methodologies necessary for controlling the morphology and structure of conducting polymers are required. The importance of viewing the properties of a conducting polymer as a complex between a charged backbone and a counterion cannot be stressed enough. For that reason the polypyrrole/toluene sulfonate system is an attractive possibility because a stable dopant polymer interaction was identified as well as establishing a means of improving the stability. If lower conductivities (without comprising environmental stability) are desired, one must consider multi-component systems in which the conductivity of the system is controlled by the ratio of conducting components to non-conducting components. A decreasing of the conductivity by reducing the degree of oxidation of the backbone would result in the decreasing of the environmental stability of the polypyrrole. This is because neutral polypyrrole reacts with oxygen and water. In addition, in order to have complete control over the morphology and structure of the multicomponent system, it is necessary that the materials be post processible. Finally whether an electrochemical or chemical approach towards the synthesis of multicomponent systems is undertaken, one must carefully consider the method by which the polymer is rendered conducting and the role of the counterion in determining the ultimate reactivity of these materials in an inert atmosphere and in the ambient environment. The realization of a stable, processible, conducting polymer with tailorable electrical properties will only occur as a result of engineering on the molecular level. For that reason polypyrrole/toluene sulfonate is only a first step towards that goal. Further research must evolve from this point.

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